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Structure and calculation of field-induced free-free transition matrix elements in many-electron atoms

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In earlier work [Phys. Rev. A **65**, 043412 (2002)] we examined the description of atom-radiation coupling in terms of the multipolar Hamiltonian rather than the minimal coupling one, and reached the conclusion that the simple operator $D_{SF}(r) = \{ {r,\ r < r_0 \atop r_0,\ r \geqslant r_0}$ constitutes a good approximation to the full electric interaction, H_{el}. Unlike the standard length form of the electric dipole approximation (EDA), $D_{SF}(r)$ does not increase indefinitely. Instead, it stops at $r_0 = 3\lambda/8$, where λ is the wavelength, and then remains constant. This theoretically founded simplification of H_{el} has obvious computational advantages over H_{el}, while at the same time accounts for effects beyond the EDA. The present paper discusses the elucidation of the singularities of the free-free matrix elements using $D_{SF}(r)$ and state-specific, energy-normalized, numerical scattering functions in polyelectronic atoms, and explains how their computation can be done efficiently. Accurate knowledge of such matrix elements is critical to the quantitative solution of time-dependent or time-independent problems involving various multiphoton processes that are induced by strong fields and involve off-resonance coupling between extended wave functions representing high-n Rydberg states of the discrete spectrum or asymptotically unbound states of the continuum. For completeness, the singularities of the EDA are also derived and discussed within the present approach.

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I. INTRODUCTION

A. Nonperturbative solution of the time-dependent Schrödinger equation

The impressive developments in the science and technology of preparation and control of strong or/and short radiation pulses (SSRPs) of a very broad spectrum of wavelengths, from the infrared to the soft x-ray region, gave birth to a fundamentally new time-dependent many-electron problem (TDMEP): that of having to solve from first principles the time-dependent Schrödinger equation (TDSE) nonperturbatively, for situations where an initial ground or excited atomic or molecular state with an arbitrary polyelectronic structure interacts with one or more SSRPs. Such interactions induce absorption of one or more photons, with the system normally undergoing transition to the continuous spectrum of one or more free particles. When the field is strong, the evolution of the system and the concomitant phenomena (e.g., above threshold ionization) depend not only on on-resonance absorption of photons inside the continuum, but also on off-resonance couplings.

Even though there has been progress in the understanding of fundamental processes using simple models and formal simplifications, the fact remains that, apart from basic phenomenology, the complete and quantitative aspects of the atomic (molecular) physics depends on the interplay of the characteristics of the pulse(s) with the energies and with the actual electronic structures and interchannel couplings of the free-atom (molecule) states in the discrete and in the continuous spectrum. (For molecules, the TDMEP may be accompanied by considerations of possible processes due to vibration, rotation, and fragmentation.)

Given the challenge of the aforementioned TDMEP, two decades ago we argued and started demonstrating on prototypical systems that such TDMEPs can be solved efficiently and reliably via the standard expansion approach, provided that the wave functions are chosen so as to correspond accurately to the physical states of the discrete and of the continuous spectrum. The method was named the state-specific expansion approach (SSEA) [1,2]. Here, we recall its essence in order to set the stage for the justification and results of the present work. We are concerned with the field-induced evolution over electronic states only, with implementation to atomic electronic structures.

The starting point is the formal expansion of $|\Psi(t)\rangle$ in a complete N-electron, multichannel function space of stationary states in the discrete and in the continuous spectrum. The key feature and argument of the SSEA is to use, in conjunction with the problem of interest, reliable as well as manageable state-specific N-electron wave functions, i.e., wave functions that have been obtained in direct correspondence with the electronic structure of each discrete, $|m\rangle$, or scattering, $|\varepsilon\rangle$, state, in terms of which $|\Psi(t)\rangle$ is expressed as (we omit the index for each possible channel)

$$|\Psi(t)\rangle = \sum_m a_m(t)\,|m\rangle + \int_0 b_\varepsilon(t)\,|\varepsilon\rangle\, d\varepsilon. \tag{1}$$

Each wave function in Eq. (1) has its own symmetry and radial characteristics, with most of them belonging to sets that are known as perturbed or unperturbed channels. The channel is defined by the series of same-symmetry Rydberg and scattering wave functions. Normally, we compute their outer orbital numerically by the fixed-core, term-dependent Hartree-Fock method. (When necessary and possible, the core includes the significant near-degeneracy correlation effects). In

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this way, one obtains a structure-dependent N-electron basis set where intrachannel coupling is eliminated.

In all problems requiring the determination of $|\Psi(t)\rangle$ nonperturbatively, i.e., requiring the solution of the TDSE to all orders of perturbation theory, in principle *all* of the terms in Eq. (1) which are allowed by the symmetry of the total, time-dependent Hamiltonian are coupled. The significance of their direct or indirect contribution to a particular property or phenomenon depends on the characteristics of the problem.

The symbols $|m\rangle$ represent bound N-electron state-specific wave functions. Based on their zero-order configurational labels, these represent valence and low- and high-lying Rydberg states, as well as multiply excited and inner-hole states. Electron correlation is incorporated judiciously in terms of methods of multiconfigurational Hartree-Fock (MCHF) and of configuration interaction with optimized orbitals [3].

The symbols $|\varepsilon\rangle$ represent energy-normalized scattering states (also called free or continuum states). ε is the energy of the free electron above the threshold of the channel. In practice, their number is large (in the many thousands), and emerges directly from the chosen range of the energy inside the continuous spectrum and from the size of the energy step inside this range. The final values of these parameters are chosen having as criteria the accurate evaluation of integrals, reliable convergence, and the economy of the overall computation. The use of numerically accurate, energy-normalized, channel-dependent basis sets of electron scattering functions, which satisfy the proper boundary conditions in the asymptotic region, secures flexibility as well as reliability to the overall calculation of $|\Psi(t)\rangle$, and of properties such as time-dependent transition probabilities and photoelectron angular distributions. At the same time, as explained below, it requires special handling of free-free transition matrix elements, especially when the two energy states are nearly or exactly degenerate.

The emphasis on carrying out state-specific calculations of wave functions, using, depending on the case, polyelectronic theory and appropriate computational methods, e.g., Refs. [1–3], has serious advantages in the quest for the reliable solution of TDMEPs. In the context of the present topic, we mention two of them:

(1) It is clear that the characteristics of, say, a compact and strongly correlated doubly excited state, regardless of its position in the energy spectrum, are very different from those of Rydberg states, whose outer orbital may extend to thousands of atomic units with very many oscillations and nodes. Therefore, if a TDMEP requires consideration of both types, it is evident that a common fixed one-electron basis set (e.g., "Gaussians," Slater type, or B splines) cannot represent them reliably in a tractable way. The same holds, in general, when basis sets are used for the representation of the states in the continuous spectrum of multielectron systems. This spectrum is not smooth, except for possible restricted regions. On the contrary, it is normally perturbed both by interchannel coupling and by the presence of unstable states (resonances) whose electronic structure (multiply or inner-hole excited) requires the use of different function spaces than those which can represent, to some approximation, the smooth continuum.

(2) By using energy-normalized wave functions with the rigorous asymptotic boundary conditions, instead of approximations to them represented by expansions in terms of box-normalized fixed basis sets, it is possible to understand and handle systematically the structure of the diagonal free-free matrix elements (see below) and, consequently, to avoid possible failures in the quantitative computation of observables [4].

B. Matrix elements

The substitution of the form (1) into the TDSE converts it into a system of coupled integro-differential equations, whose numerical solution produces the complex time-dependent mixing coefficients $a_m(t)$ and $b_\varepsilon(t)$, whose absolute value squared, $|a_m(t)|^2$ and $|b_\varepsilon(t)|^2 d\varepsilon$, defines directly the occupation probability of each corresponding stationary energy state, provided one uses the electric field gauge or chooses the solution $|\Psi(t)\rangle$ at the points of time over a field cycle where the vector potential $\vec{\boldsymbol{A}}(t)$ vanishes [1,5].

The numerical input which is needed for the solution of the coupled equations consists of the state-specific stationary energies and of the bound-bound (b-b), bound-free (b-f), and free-free (f-f) matrix elements of the total Hamiltonian, $\boldsymbol{H}(t) = \mathbf{H} + \boldsymbol{V}(t)$. $\mathbf{H}$ is the field-free Hamiltonian and $\boldsymbol{V}(t)$ is the time-dependent interaction between the atom (molecule) and the radiation pulse.

The original formulation and implementation of the SSEA to electronic transitions [1] adopted the electric dipole approximation (EDA) to the full atom-field interaction in the velocity form, in which the coupling is $(1/c)\vec{\boldsymbol{A}}(t)\cdot\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{p}}$ is the momentum operator for the electrons and $\vec{\boldsymbol{A}}(t)$ satisfies $\vec{\nabla}\cdot\vec{\boldsymbol{A}}(t) = 0$ (Coulomb gauge), and has no dependence on $\vec{\boldsymbol{r}}$ (EDA), e.g., Ref. [6]. In view of the fact that the f-f matrix elements of the $\vec{\boldsymbol{p}}$ operator give rise to troublesome singularities as $\varepsilon' \to \varepsilon$, the calculation of the f-f integral with the fixed-core Hartree-Fock, state-specific, energy-normalized, numerical scattering orbitals was done by transforming the integrals of $\vec{\boldsymbol{p}}$ into integrals of $\sim\frac{1}{r^2}$ (acceleration form), which converge without difficulty, and by implementing a methodology that combines numerical and analytic [Wentzel-Kramers-Brillouin (WKB)] techniques [1,7].

Since the present work deals with the issue of the computation of f-f transition matrix elements in conjunction with the form of the coupling operator, it is appropriate here to recall certain facts from the background to the problem of computing rigorously and practically the f-f dipole matrix element which arises from the presence of singularities at points $\varepsilon' = \varepsilon$. Such diagonal matrix elements are necessary not only for the nonperturbative solution of the TDSE via the SSEA but also in any time-independent, high-order perturbation theory of multiphoton transitions in the continuous spectrum.

The coupling operator $(1/c)\vec{\boldsymbol{A}}(t)\cdot\vec{\boldsymbol{p}}$ is the one to which the minimal coupling atom + field Hamiltonian [i.e., the full interaction using the vector potential $\vec{\boldsymbol{A}}(\vec{\boldsymbol{r}},t)$ in the Coulomb gauge] is reduced in the EDA. On the contrary, the length operator of the EDA, $\vec{\boldsymbol{r}}$, represents the reduction of the multipolar Hamiltonian, which expresses the full electric interaction in terms of the electric field $\vec{\boldsymbol{E}}(\vec{\boldsymbol{r}},t)$ to the form $\vec{\boldsymbol{E}}(t)\cdot\vec{\boldsymbol{r}}$ [6], where $\vec{\boldsymbol{E}}(t) = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A}(t)$. Manipulation with commutators or differential equations yields a third coupling operator in the EDA, the Kramers-Henneberger (KH) frame [8], which, for a Coulomb potential, has the form $-\frac{Z}{|\vec{r}-\vec{\alpha}(t)|}$, where

$\vec{\alpha}(t) = -\frac{1}{c}\int_{-\infty}^{t} dt'\vec{A}(t')$. In lowest order of its expansion, the KH interaction gives the acceleration operator, $\frac{Z\vec{\alpha}(t)\cdot\vec{r}}{r^3}$.

Operators of the form $\frac{1}{r^q}$, with the integer $q \geqslant 2$, when used in matrix elements with Coulomb functions or, in the many-electron case, with scattering Hartree-Fock numerical functions, lead to convergent integrals, without the difficulties of singularities that characterize the length and the velocity operators. The utility of such operators for the convenient computation of f-f integrals with Coulomb functions was demonstrated long ago in the context of nuclear physics [9]. This fact was utilized decades ago by Peach [7] and, later, along the same lines, by Seaton [10,11], for the computation of off-diagonal f-f matrix elements in the EDA. Nevertheless, even in the methods used in Refs. [7,10,11], the severe difficulties of accurate and practical integration of the diagonal (equal energies) radial integral of r involving the sinusoidal asymptotic parts of the two states in the neighborhood of $\varepsilon' = \varepsilon$, where it diverges, remain. (For f-f transitions, the main formulas of Refs. [7,10,11] neglect a term which is important at large radii and at equal energies—see Sec. III). As Seaton observed, his formulas "cannot be used when $(E - E')$ is very small" (p. 2610 of Ref. [11]).

Finally, one may ponder on the implementation of the KH frame [8] (also loosely called the acceleration gauge) in order to solve the TDSE with a coupling operator which is dominated by the $1/r^2$ dependence. As already said, this dependence eliminates the troublesome singularities from the diagonal f-f dipole integrals which arise from the sinusoidal boundary condition of the energy-normalized scattering functions in the asymptotic region. The use of the KH-transformed TDSE has indeed been explored computationally by the grid method, albeit with model one-dimensional systems [12] which have very little to do with real, N-electronic structures and spectra of atoms or molecules. Of course, for the one-electron hydrogenic atom, such a nonperturbative treatment of the TDSE for strong fields is, in principle, a tractable alternative. However, for real many-electron systems this endeavor would not be convenient, or economical, or reliable. Apart from the formal requirements of practical significance, such as transformation of wave functions [8,12] so as to obtain time-dependent coefficients with the meaning of amplitudes of probability, the degree of accuracy is expected to be low and unreliable when using approximate wave functions. This is because, when used in integrals of N-electron systems with bound antisymmetrized wave functions, the KH interaction would pick up $1/r^2$-like contributions from the short-range portion of the integrand, where the wave functions of the two N-electron states must be known very accurately. A discussion on the general issue of the choice and reliability of the three EDA operators in N-electron integrals was given decades ago in connection with the calculation of oscillator strengths of one-photon transitions [13].

C. The special case of the hydrogenic atom

In the special case of the hydrogenic atom, where the field is purely Coulombic and the exact eigenfunctions are known analytically, the b-b, b-f, and f-f matrix elements were obtained already in 1929 by Gordon [14] for the dipole length form of the EDA. He did this by establishing a recursion relation that has as its reference point a known integral involving hypergeometric functions of the type $F(a,b;c;z)$. A summary of those results is given in the Appendix of Landau and Lifshitz [15] on hypergeometric functions. The derivation of this result has also been given by Alder *et al.* [9] based again on recursion relations involving hypergeometric functions.

In spite of their analytic form, Gordon's [14] formulas are not numerically free of trouble [15–21]. This fact is linked to the last argument of $F(a,b,c,z)$, which is $-\frac{4kk'}{(k+k')^2}$. As $k' \to k$ (i.e., $\varepsilon' \to \varepsilon$), this term goes to unity, and at that point this form of hypergeometric function does not converge [22].

The need to compute the length dipole integral correctly for off-diagonal and especially for diagonal ($\varepsilon' = \varepsilon$) matrix elements became prominent in the 1980's in the context of time-independent perturbation theory for multiphoton processes where free-free transitions occur. The early papers pointed out the significance of the diagonal matrix elements in the EDA, but did not tackle the mathematics of the singularity for $\varepsilon' \to \varepsilon$, even in hydrogen, e.g., Refs. [23,24]. Indeed, for the Coulomb potential this was done for the first time, at different levels, by Pan [17,18], by Madajczyk and Trippenbach [19], and by Véniard and Piraux [20]. (See also Korol's subsequent contributions [21].) They employed the EDA in hydrogen and elucidated the nature of the singularity which exists when the free-electron energies coincide in the hydrogenic integrals,

$$\langle R_\ell(\varepsilon)|\, r\, |R_{\ell\pm1}(\varepsilon')\rangle \tag{2}$$

and

$$\int_0^\infty d\varepsilon'\, \langle R_\ell(\varepsilon)|\, r\, |R_{\ell\pm1}(\varepsilon')\rangle C(\varepsilon'). \tag{3}$$

$R_\ell(\varepsilon)$ is the radial Coulomb function and $C(\varepsilon)$ is a continuous function whose first derivative exists at $\varepsilon' = \varepsilon$ [20]. We recall that the source of the irregularities in the f-f integrals is the asymptotically unbound behavior of the wave functions in conjunction with the form of the operator. Our work in Refs. [1,2,4] on the nonperturbative solution of the many-electron TDSE had to face this problem when numerical scattering functions, computed with a fixed-core, term-dependent potential, are employed.

Finally, it is worth adding that, as in various problems of scattering theory, the results of Refs. [19–21] were obtained with the help of the introduction inside integrals of a convergence factor, such as $e^{-\xi r}$, with $\xi \to 0$ in the final formulas. In the computational context an alternative type of regularization procedure for eliminating the divergence in f-f dipole length integrals caused by the asymptotic form of the free-electron wave function has been explored by Gao and Starace [25] and by Chrysos and Fumeron [26]. They implemented exterior complex scaling, a technique which was initially introduced in atomic physics for the regularization of resonance eigenfunctions [27,28], and argued that "the exact value of the integral is defined by a cusp, loop or inflection on a well-defined θ-trajectory, analogously with resonance quantization" (p. 3118 of Ref. [26]). The numerical results that were presented in Refs. [25,26] were obtained for pairs of different energies. It is a moot point whether such procedures will be economical and/or practical for the reliable computation and handling of dipole integrals for the same, or nearly the same, energy states.

D. The cases of polyelectronic structures and of the full atom-radiation interaction

In contradistinction to the special case of the hydrogen atom, when tackling TDMEPs the one-electron scattering functions are not known analytically. Instead, methods have been developed where they are computed either numerically in the physically determined potential and with rigorous asymptotic boundary conditions, or, in terms of an expansion in some type of finite basis set with imposed box normalization. The latter approach, apart from having limitations and disadvantages when it comes to dealing with arbitrary polyelectronic structures where multichannel coupling occurs and where resonances are embedded in the scattering continuum, does not guarantee the accurate accounting of the effects of the singularities when $\varepsilon' \approx \varepsilon$ or $\varepsilon' = \varepsilon$, especially when both ε' and ε are very close to threshold [4].

Furthermore, there is an issue which has hardly been addressed in practice, with the exception of the work reported in Refs. [29–32]. Specifically, it was pointed out that the EDA cannot be justified *a priori* for matrix elements involving wave functions of very large range (e.g., Rydberg levels with large quantum numbers), or of unlimited range, as are the state-specific energy-normalized scattering wave functions. In view of this uncertainty, we developed a theory [30–32] for the practical implementation of the full atom-radiation interaction, in the multipolar Hamiltonian formalism [6]. The first term of the expansion of this Hamiltonian produces the dipole interaction in the length form [6]. In an application to the excitation of Rydberg wave packets in the hydrogen atom [32], it was shown that "off-resonance couplings lead to differences between the full-interaction operator and the EDA which cannot be neglected. In the extreme case of intrashell couplings for the $n = 50$ shell, calculation shows that the $50p$ state is coupled to angular momentum states up to $\ell = 21$, compared to the electric dipole coupling of $\Delta\ell = \pm 1$" (abstract of Ref. [32]).

In the work reported here, we investigated the rigorous as well as practical computation of f-f matrix elements such as those of Eqs. (2) and (3), except that now this computation engages the full electric interaction operator in the simplified form that was introduced in Refs. [30,32]—see the next section. This operator [Eq. (9)] is finite at infinity and its singularities exhibit the features of those of the EDA velocity operator, which have the form

$$\mathrm{P}\frac{f_1(\varepsilon,\varepsilon')}{\varepsilon - \varepsilon'} + f_2(\varepsilon,\varepsilon)\delta(\varepsilon - \varepsilon'), \tag{4}$$

where the functions f_1 and f_2 are smooth functions and P stands for principal value.

Expressions such as (4) are much simpler to handle numerically than that which is produced by the EDA length operator. The conclusions also hold for Rydberg-free matrix elements, where the Rydberg wave function is very extended and its turning point is way beyond the limiting radius r_0 [Eq. (10)], whose value is established by theory [30,32].

II. STATEMENT OF THE PROBLEM

As regards the mathematical exploration of the singularities of the diagonal field-induced coupling matrix elements, it is sufficient to consider only the contribution from the asymptotic part of the eigenfunctions. However, this is not enough for the accurate computation of matrix elements such as those of Eqs. (2) and (3) in polyelectronic systems. Instead, this computation requires accurate knowledge of the two energy-normalized scattering wave functions over the whole range of the radius as obtained numerically in the field of a term-dependent potential. This is critical for the calculation of the energy integrals of the type (3), which are the ones entering the procedure of integration of the TDSE. We note that, in the case studied here, these integrals involve a coupling operator which represents the full electric interaction operator in a simplified form—see below.

As an example, we cite Korol's [21] discussion and results for the structure of the diagonal singularity of the EDA f-f matrix elements, using the model potential $V(r) = V_0(r) - \frac{Z}{r}$, where $V_0(r)$ is a short-range potential. He used the asymptotic form of the Coulomb function, to which a phase shift due to $V_0(r)$ can be added. The model assumes that the asymptotic form of the Coulomb functions starts beyond the point where $V_0(r)$ is zero. When it comes to the *ab initio* calculation of matrix elements, this assumption is not generally helpful, since, especially for small energies and/or large angular momenta, the exact wave function differs significantly from the asymptotic behavior. Figure 1 provides an example of the difference between the exact hydrogenic wave function and its asymptotic form for $\ell = 30$. This difference is evident from the inspection of the WKB formula (D3) of Appendix D as compared with Eq. (15).

A. The simplified form of the full electric operator

Apart from the issue of having to handle f-f matrix elements with energy-normalized scattering functions, or b-b

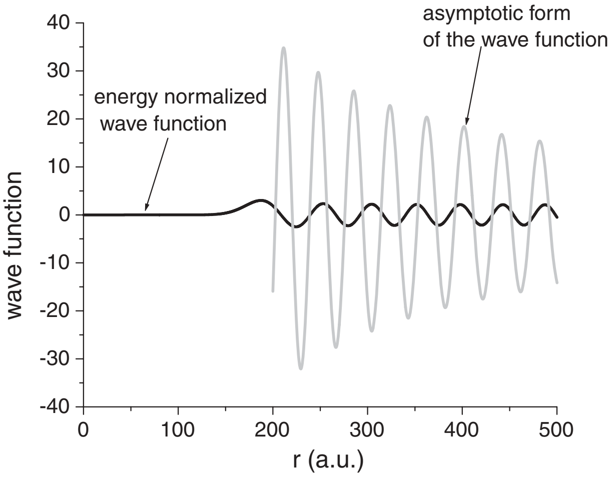

FIG. 1. The energy normalized scattering wave function of the hydrogen atom (solid black line), for angular momentum $\ell = 30$ and energy 0.01 a.u., compared to its asymptotic form given in Eq. (15) (solid light gray line).

and b-f integrals with extended state-specific Rydberg orbitals, obtained numerically, the aim of the work reported here was to understand the mathematical structure of these matrix elements when a different coupling operator is used. This operator accounts for effects beyond the EDA. It has emerged from the judicious simplification of the full electric interaction of the multipolar Hamiltonian (see below) and, because of its simple form, constitutes a computationally practical tool, in distinct contrast to the case of the exact form of the full electric interaction operator.

The electric part of the multipolar Hamiltonian can be written as [6]

$$H_{\mathrm{el}} = e \sum_j \int_0^1 \vec{r}_j \cdot \vec{E}(\lambda\vec{\kappa} \cdot \vec{r}_j)\, d\lambda, \tag{5}$$

where $\vec{\kappa}$ is the wave vector of the radiation and $\vec{E}$ is the electric field.

Assuming a plane-wave form for the electric field and taking its polarization along the x axis, while the z axis is chosen in the direction of $\vec{\kappa}$, we have obtained an expression of the above Hamiltonian in terms of integrals of spherical Bessel functions multiplied by an angular part containing the $Y_\ell^{\pm 1}(\theta,\varphi)$ spherical harmonics [30,32]. Specifically [see Eqs. (A5) and (6) of Ref. [30], the radial parts are given by

$$(2\ell+1)F_\ell(r) = \frac{(2\ell+1)}{\kappa} \int_0^r dr' \frac{1}{r'} j_\ell(\kappa r'), \tag{6}$$

where κ is the wave number and $j_\ell(r)$ is the regular spherical Bessel function.

The present work is concerned with the first term of the expansion, defined by $\ell = 1$. We call this term the dipole coupling part of the full operator. For small values of its argument, $j_\ell(x) \approx \frac{x^\ell}{(2\ell+1)!!}$. Substituting this expression into the above integral for $\ell = 1$ we obtain the usual dipole length form, $3F_1 \approx r$. On the other hand, for large values of its argument, the function $F_\ell(r)$ becomes [30]

$$F_\ell(r) \to \frac{1}{\kappa} c_\ell - \frac{1}{\kappa^2} \int_r^\infty dr' \frac{1}{r'^2} \sin(\kappa r' - \ell\pi/2), \tag{7}$$

where c_ℓ is the value of the integral from 0 to ∞:

$$c_\ell = \frac{\sqrt{\pi}\,\Gamma(\ell/2)}{2(\ell+1)\Gamma(\ell/2+1/2)}. \tag{8}$$

Γ is the gamma function. For $\ell = 1$ one has $c_1 = \pi/4$.

Thus, we reach the conclusion that for sufficiently large values of r, the operator F_ℓ reaches a constant value, and this is true for all values of ℓ. This is in contrast to the EDA (small κ), where the values of the length operator increase indefinitely.

Based on such results, we suggested [30] the use of a different operator for practical calculations, which is a simplified form of the dipole coupling part of the full electric operator and is strongly suggested by the plot of $3F_1$ (Fig. 2). This operator is

$$D_{SF}(r) = \begin{cases} r, & r < r_0, \\ r_0, & r \geqslant r_0, \end{cases} \tag{9}$$

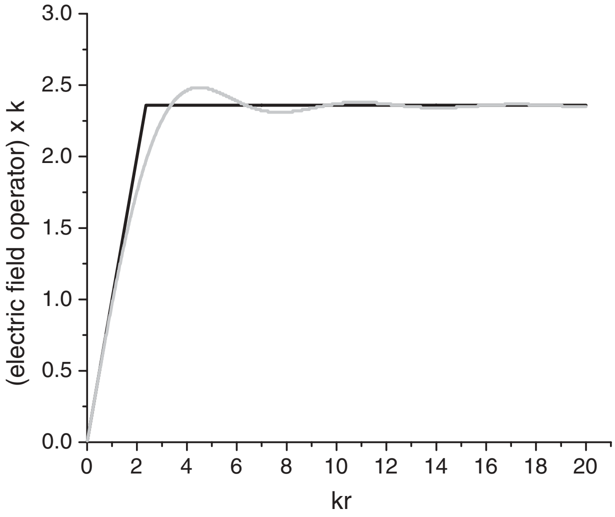

FIG. 2. Plot of the full electric operator $3F_1$, Eq. (6), for $\ell = 1$ (solid light gray line) vs the model operator of Eq. (9) (solid black line), both multiplied by the photon wave number k.

where the value of r_0 depends on the wave number of the radiation, through the relation

$$r_0 = 3\pi/4\kappa = 3\lambda/8. \tag{10}$$

In words, the operator $D_{SF}(r)$ has the length form up to a point r_0, which is determined by the wavelength of the radiation, and remains constant from then on. For example, for radiation of wavelengths 400 or 10 nm, the corresponding limits are $r_0 \approx 2830$ a.u. or $r_0 \approx 71$ a.u. We recall that the mean value of r for the $7p$ orbital of hydrogen is 72.5 a.u. Hence, it is evident that, for problems of multiphoton processes induced by strong fields, where the coupling requires the consideration of all types of matrix elements, on and off resonance, such data indicate that the EDA often may be inadequate when pairs of Rydberg or of scattering states need to be coupled [30–32].

In the next section, we give the theory for the structure and calculation of matrix elements involving the operator $D_{SF}(r)$, Eq. (9), as well as those involving EDA, so that a comparison between the two operators can be made.

III. THEORY

We consider the radial integral of $D_{SF}(r)$ and write

$$\int_0^\infty dr\, y_{kl} D_{SF}(r) y_{k'l'} = \int_0^{r_0} dr\, y_{kl}\, r\, y_{k'l'} + r_0 \int_{r_0}^\infty dr\, y_{kl} y_{k'l'}, \tag{11}$$

where l is the angular momentum quantum number.

For a nonhydrogenic atom, the first integral is calculated numerically up to a radius r_c, beyond which the core orbitals are not important. In most cases of wavelengths, r_c is smaller than r_0. Consequently, the rest of the integral, as well as the second one, involves functions resembling the hydrogenic ones. We write this part as

$$\int_{r_c}^\infty dr\, y_{kl} D_{SF}(r) y_{k'l'} = D_{kl;k'l'}(r_c,r_0) + r_0 S_{kl;k'l'}(r_0). \tag{12}$$

The overlap $S_{kl;k'l'}(r_0)$ is the subject of Appendix A, while the dipole matrix element $D_{kl;k'l'}(r_c,r)$ is analyzed below [see Eq. (18)]. For $r \to \infty$, the asymptotic form of the wave function for $k > 0$ is

$$y_{kl} = \sqrt{\frac{2}{\pi k}} \sin\left(kr + \frac{Z}{k}\ln r + \delta_{kl}\right) + O\left(\frac{1}{r}\right), \tag{13a}$$

where

$$\delta_{kl} = \sigma_l(k) + \frac{Z}{k}\ln k - l\pi/2 + \delta^v_{kl}. \tag{13b}$$

$\sigma_l(k)$ is the Coulomb phase shift and δ^v_{kl} is the additional phase shift caused by the nonhydrogenic terms. The above wave function is energy normalized in the sense

$$\int_0^\infty dr\, y_{kl}\, y_{k'l'} = \frac{1}{k}\delta(k-k') = \delta(\varepsilon-\varepsilon'). \tag{14}$$

As regards the normalization of Eq. (14), we note that the literature contains a few types of normalization for the wave functions of the continuous spectrum. The condition of Eq. (14) is the most appropriate one, since it leads to wave functions that are finite at the ionization threshold $\varepsilon = 0$ (see Appendix D).

For the analysis of the problem in terms of the dipole operator, a more accurate form of the asymptotic expression of y_{kl} is needed. This is given by

$$y_{kl} = \sqrt{\frac{2}{\pi k}}\left(1 - \frac{a_k}{r}\right) \sin\left(kr + \frac{Z}{k}\ln r + \delta_{kl}\right) + \sqrt{\frac{2}{\pi k}}\frac{b_{kl}}{r}\cos\left(kr + \frac{Z}{k}\ln r + \delta_{kl}\right) + O\left(\frac{1}{r^2}\right), \tag{15}$$

where

$$a_k = \frac{Z}{2k^2} \quad \text{and} \quad b_{kl} = \frac{l(l+1) + (Z/k)^2}{2k}. \tag{16}$$

Expression (15) can be obtained either from the confluent hypergeometric function or, more generally, from the WKB wave function (see Appendix D).

Below we shall derive the form of a matrix element of the EDA length operator involving functions of the continuous energy spectrum. We compare the singular part of the matrix element at equal energies with the expression derived by other investigators who employed analytic Coulomb wave functions. We then describe the modifications resulting from the use of $D_{SF}(r)$, Eq. (9).

A. Matrix elements between positive-energy wave functions

For values of the radial distance r larger than r_c, where the effect of core orbitals becomes negligible, any one-electron model of the atomic Hamiltonian assumes the hydrogenic form. Years ago, Peach [7] derived a procedure for the calculation of the dipole matrix element for $r > r_c$,

$$D_{kl;k'l'}(r_c,r) \equiv \int_{r_c}^{r} dr\, y_{kl}\, r\, y_{k'l'}, \tag{17}$$

which she expressed as

$$(\varepsilon-\varepsilon')^2 D_{kl;k'l'}(r_c,r) = \int_{r_c}^{r} dr \frac{Z}{r^2} y_{kl}\, y_{k'l'} - [X_{kl;k'l'}(r) + (\varepsilon-\varepsilon') r\, W_{kl;k'l'}(r)]^r_{r_c}. \tag{18}$$

Here, X is defined as the function

$$X_{kl;k'l'}(r) = \frac{1}{2}\left[\frac{D_{ll'}}{r^2} - \frac{2Z}{r} - (\varepsilon+\varepsilon')\right] y_{kl}\, y_{k'l'} - \frac{1}{2}\frac{dy_{kl}}{dr}\frac{dy_{k'l'}}{dr} + \frac{C_{ll'}}{r} W_{kl;k'l'}(r), \tag{19}$$

with

$$D_{ll'} = \tfrac{1}{2}l(l+1) + \tfrac{1}{2}l'(l'+1) \quad \text{and} \quad C_{ll'} = \tfrac{1}{2}l(l+1) - \tfrac{1}{2}l'(l'+1). \tag{20}$$

Also, the function $W_{kl;k'l'}(r)$ is defined [see Appendix A, Eq. (A7)] as

$$W_{kl;k'l'}(r) \equiv \frac{1}{2}\left[y_{k'l'}\frac{d}{dr}y_{kl} - y_{kl}\frac{d}{dr}y_{k'l'}\right]. \tag{21}$$

We point out that the quantities $X_{kl;k'l'}$ and $W_{kl;k'l'}$ vary wildly as functions of energy, and this implies the exercise of caution when they are used as integrands. This behavior is made explicit by invoking the WKB form of the wave functions in Appendix D.

In Appendix A, a procedure similar to the one of Peach [7] is used to derive the overlap between two positive energy wave functions. Using the integral

$$S^{-2}_{kl;k'l'}(r) \equiv \int_r^\infty dr' \frac{1}{r'^2} y_{kl}\, y_{k'l'} \tag{22}$$

introduced in Eq. (A6) and discussed in Appendix B for wave functions having reached their asymptotic behavior, Eq. (18) is written in a symmetrical form as

$$\begin{aligned}(\varepsilon-\varepsilon')^2 D_{kl;k'l'}(r_c,r) &= Z S^{-2}_{kl;k'l'}(r_c) + X_{kl;k'l'}(r_c) - Z S^{-2}_{kl;k'l'}(r) - X_{kl;k'l'}(r) \\ &\quad + (\varepsilon-\varepsilon')[r_c W_{kl;k'l'}(r_c) - r W_{kl;k'l'}(r)].\end{aligned} \tag{23}$$

The above expression requires that at $k = k'$,

$$Z S^{-2}_{kl;kl'}(r_c) + X_{kl;kl'}(r_c) = Z S^{-2}_{kl;kl'}(r) + X_{kl;kl'}(r) \tag{24}$$

and

$$\begin{aligned}&\frac{\partial}{k\partial k}\left[Z S^{-2}_{kl;k'l'}(r_c) + X_{kl;k'l'}(r_c)\right]_{k\to k'} + r_c W_{kl;kl'}(r_c) \\ &\quad = \frac{\partial}{k\partial k}\left[Z S^{-2}_{kl;k'l'}(r) + X_{kl;k'l'}(r)\right]_{k\to k'} + r W_{kl;kl'}(r).\end{aligned} \tag{25}$$

The limit $k \to k'$ is indicated in Eq. (25) because $\frac{\partial}{\partial k} S^{-2}_{kl;k'l'}(r)$ is singular at $k = k'$ [see Eq. (B13)]. Since the same expression appears on both sides of Eqs. (24) and (25) for two different values of r, we conclude that, in the limit $k \to k'$, the expressions are independent of this variable. Given that the wave functions take the form of simple trigonometric functions at very large distances, we need only to examine the quantities on the right-hand side of the above expressions in the limit $r \to \infty$.

We point out that in Eq. (34) of Ref. [7], which is the analog of our Eq. (18), in the limit $r \to \infty$ the expression in the brackets is considered to be zero. In the context of a rigorous treatment, this is incorrect. In fact, this term, which is also omitted in Seaton's treatment [10,11], gives rise to the principal values and δ functions of Eq. (49) whose contribution to the computation of the diagonal f-f matrix elements cannot be ignored.

Substituting in Eq. (19) the asymptotic form of y given by Eq. (13), we obtain

$$\begin{aligned}\lim_{r\to\infty} X_{kl;k'l'}(r) = &-\frac{(k+k')^2}{4\pi\sqrt{kk'}}\lim_{R\to\infty}\cos[(k-k')R+\delta_{kl}-\delta_{k'l'}]\\ &+\frac{(k-k')^2}{4\pi\sqrt{kk'}}\lim_{R\to\infty}\cos[(k+k')R+\delta_{kl}+\delta_{k'l'}],\end{aligned} \tag{26}$$

where we put $R = r - \frac{Z}{kk'}\ln r$, as in Appendix A. Note that $\lim_{r\to\infty} S^{-2}_{kl;kl'}(r) = 0$. Then, at $k = k'$, Eq. (24) takes the form

$$Z\,S^{-2}_{kl;kl'}(r_c) + X_{kl;kl'}(r_c) = -\frac{k}{\pi}\cos(\delta_{kl}-\delta_{kl'}). \tag{27}$$

Taking the derivative of Eq. (26) with respect to k we have

$$\begin{aligned}\lim_{r\to\infty}\frac{\partial}{\partial k}X_{kl;k'l'}(r) = &\frac{(k+k')^2}{4\pi\sqrt{kk'}}\left(R+\frac{\partial\delta_{kl}}{\partial k}\right)\lim_{R\to\infty}\sin[(k-k')R+\delta_{kl}-\delta_{k'l'}] - \frac{(k+k')}{2\pi\sqrt{kk'}}\lim_{R\to\infty}\cos[(k-k')R+\delta_{kl}-\delta_{k'l'}]\\ &-\frac{(k-k')^2}{4\pi\sqrt{kk'}}\left(R+\frac{\partial\delta_{kl}}{\partial k}\right)\lim_{R\to\infty}\sin[(k+k')R+\delta_{kl}+\delta_{k'l'}] + \frac{(k-k')}{2\pi\sqrt{kk'}}\lim_{R\to\infty}\cos[(k+k')R+\delta_{kl}+\delta_{k'l'}]\\ &-\frac{1}{2k}X_{kl;k'l'}(r),\end{aligned} \tag{28}$$

which gives, for the energy derivative at $k = k'$,

$$\begin{aligned}\lim_{r\to\infty}&\frac{\partial}{k\partial k}[X_{kl;k'l'}(r)]_{k=k'}\\ &= \left(r-\frac{Z}{k^2}\ln r+\frac{\partial\delta_{kl}}{\partial k}\right)\frac{1}{\pi}\sin(\delta_{kl}-\delta_{kl'})\\ &\quad-\frac{1}{\pi k}\cos(\delta_{kl}-\delta_{kl'})-\frac{1}{2k^2}X_{kl;k'l'}(r).\end{aligned} \tag{29}$$

From Appendix B we obtain

$$\begin{aligned}\lim_{k\to k'}&\frac{\partial}{k\partial k}Z S^{-2}_{kl;k'l'}(r)\\ &= -\frac{Z}{2k^2}\operatorname{sgn}(k-k')\cos(\delta_{kl}-\delta_{kl'})\\ &\quad+\frac{Z}{\pi k^2}[\gamma+\ln|k-k'|+\ln r]\sin(\delta_{kl}-\delta_{kl'})\\ &\quad-\frac{Z}{2k^2}S^{-2}_{kl;kl'}(r)+O\left(\frac{1}{r^2}\right).\end{aligned} \tag{30}$$

The coefficient $-1/2$ of the last term in Eqs. (29) and (30) is peculiar to the energy-normalized wave function. [In general the asymptotic form (13a) involves a factor k^{-q}, where $q = 0$, $1/2$, or 1.] Note that the term containing the $\ln r$ in Eq. (30) cancels the corresponding term in Eq. (29). The cancellation of the r term comes from the $W_{kl;k'l'}(r)$ term in Eq. (25). Let

$$\lim_{r\to\infty} W_{kl;k'l'}(r) = W^{(0)}_{kl;k'l'}(r) + \frac{1}{r}W^{(-1)}_{kl;k'l'}(r). \tag{31}$$

Using the limiting form (15) in the definition (21), we get

$$\begin{aligned}W^{(0)}_{kl;k'l'}(r) = &-\frac{(k+k')}{2\pi\sqrt{kk'}}\lim_{R\to\infty}\sin[(k-k')R+\delta_{kl}-\delta_{k'l'}]\\ &+\frac{(k-k')}{2\pi\sqrt{kk'}}\lim_{R\to\infty}\sin[(k+k')R+\delta_{kl}+\delta_{k'l'}]\end{aligned} \tag{32}$$

and

$$\begin{aligned}W^{(-1)}_{kl;k'l'}(r) = &-\frac{(k+k')}{2\pi\sqrt{kk'}}(b_{kl}-b_{k'l'})\\ &\times\lim_{R\to\infty}\cos[(k-k')R+\delta_{kl}-\delta_{k'l'}]\\ &+\frac{(k-k')}{2\pi\sqrt{kk'}}(b_{kl}+b_{k'l'})\\ &\times\lim_{R\to\infty}\cos[(k+k')R+\delta_{kl}+\delta_{k'l'}],\end{aligned} \tag{33}$$

where, according to the definition (16),

$$\begin{aligned}b_{kl}\mp b_{k'l'} = &(k\pm k')\frac{C_{ll'}}{2kk'}+(k\mp k')\\ &\times\left[\frac{D_{ll'}}{2kk'}+\frac{Z^2}{2kk'}u(k,\pm k')\right],\end{aligned} \tag{34}$$

and u is a function whose exact form is not important. Thus,

$$\lim_{r\to\infty} r W_{kl;kl'}(r) = -\frac{r}{\pi}\sin(\delta_{kl}-\delta_{kl'})-\frac{C_{ll'}}{\pi k}\cos(\delta_{kl}-\delta_{kl'}). \tag{35}$$

Adding (29)–(31) we finally derive an expression that is independent of the variable r:

$$\begin{aligned}\frac{\partial}{k\partial k}&\left[Z S^{-2}_{kl;k'l'}(r_c)+X_{kl;k'l'}(r_c)\right]_{k\to k'}+r_c W_{kl;kl'}(r_c)\\&=-\left(\frac{1}{2}+C_{ll'}\right)\frac{1}{\pi k}\cos(\delta_{kl}-\delta_{kl'})+\frac{\partial\delta_{kl}}{\partial k}\frac{1}{\pi}\sin(\delta_{kl}-\delta_{kl'})\\&\quad-\frac{Z}{\pi k^2}\operatorname{sgn}(k-k')\cos(\delta_{kl}-\delta_{kl'})\\&\quad+\frac{Z}{\pi k^2}[\gamma+\ln|k-k'|]\sin(\delta_{kl}-\delta_{kl'}).\end{aligned}\tag{36}$$

In order to compare with expressions derived in Refs. [19,20], we must produce expressions for $\frac{\partial\delta_{kl}}{\partial k}$ as well as for the sine and cosine of $\delta_{kl}-\delta_{kl'}$.

To this purpose, we differentiate the r-independent part of the phase δ_{kl}, as given by Eq. (13b), to obtain

$$\frac{\partial\delta_{kl}}{\partial k}=\frac{\partial\sigma_l(k)}{\partial k}-\frac{Z}{k^2}\ln 2k+\frac{Z}{k^2}+\frac{\partial\delta^v_{kl}}{\partial k}.\tag{37}$$

The Coulomb phase shift is expressed as the argument of the Γ function,

$$\sigma_l(k)=\arg\Gamma\left(l+1-i\frac{Z}{k}\right)\equiv\operatorname{Im}\left\{\ln\left[\Gamma\left(l+1-i\frac{Z}{k}\right)\right]\right\}.\tag{38}$$

Therefore,

$$\frac{\partial\sigma_l(k)}{\partial k}=\frac{Z}{k^2}\operatorname{Re}\left\{\psi\left(l+1-i\frac{Z}{k}\right)\right\},\tag{39}$$

where $\psi(z)=\frac{d}{dz}\ln\Gamma(z)$ is the digamma function. Furthermore,

$$\sigma_l(k)=\sigma_0(k)-\sum_{s=1}^{l}\tan^{-1}\left(\frac{Z}{ks}\right).\tag{40}$$

In what follows we specialize the formulas for the case $l'=l\pm 1$.

Then, for $l_>=\max(l,l\pm 1)$, we get

$$\sigma_l(k)-\sigma_{l\pm 1}(k)=\pm\tan^{-1}\left(\frac{Z}{kl_>}\right).\tag{41}$$

Therefore,

$$\delta_{kl}-\delta_{kl\pm 1}=\pm\tan^{-1}\left(\frac{Z}{kl_>}\right)\pm\frac{\pi}{2}+\delta^v_{kl}-\delta^v_{kl\pm 1}.\tag{42}$$

Then,

$$\begin{aligned}\cos(\delta_{kl}-\delta_{kl\pm 1})&=-\frac{Z/k}{\left|l_>+i\frac{Z}{k}\right|}\cos\left(\delta^v_{kl}-\delta^v_{kl\pm 1}\right)\\&\quad\mp\frac{l_>}{\left|l_>+i\frac{Z}{k}\right|}\sin\left(\delta^v_{kl}-\delta^v_{kl\pm 1}\right),\end{aligned}\tag{43a}$$

$$\begin{aligned}\sin(\delta_{kl}-\delta_{kl\pm 1})&=\pm\frac{l_>}{\left|l_>+i\frac{Z}{k}\right|}\cos\left(\delta^v_{kl}-\delta^v_{kl\pm 1}\right)\\&\quad-\frac{Z/k}{\left|l_>+i\frac{Z}{k}\right|}\sin\left(\delta^v_{kl}-\delta^v_{kl\pm 1}\right).\end{aligned}\tag{43b}$$

The above expressions may be summarized as

$$\exp[i(\delta_{kl}-\delta_{kl\pm 1})]=\pm i\frac{l_>\pm i\frac{Z}{k}}{\left|l_>+i\frac{Z}{k}\right|}\exp\left[i\left(\delta^v_{kl}-\delta^v_{kl\pm 1}\right)\right].\tag{44}$$

This form is the same as the ones of Eqs. (3.2) and (3.8) of Ref. [20], remembering that for hydrogen the phase shifts δ^v_{kl} are zero. The additional phase shifts in Eq. (44) are due to the core. Note also that $C_{ll\pm 1}=\mp l_>$ in Eqs. (34)–(36).

Now, we express the dipole matrix element of Eq. (23) in terms of its two components:

$$D_{kl;k'l'}(r_c,r)\equiv D_{kl;k'l'}(r_c)-D_{kl;k'l'}(r),\tag{45}$$

where

$$\begin{aligned}D_{kl;k'l'}(r)=&\frac{1}{(\varepsilon-\varepsilon')^2}\left[Z S^{-2}_{kl;k'l'}(r)+X_{kl;k'l'}(r)\right]\\&+\frac{1}{\varepsilon-\varepsilon'}r W_{kl;k'l'}(r).\end{aligned}\tag{46}$$

As we have shown above, the matrix elements are finite at $\varepsilon=\varepsilon'$ for finite values of r. Below, we shall examine two cases: (a) $r\to\infty$ and (b) $r=r_0$. r_0 is defined in Eq. (10). In both cases, it is convenient to write the matrix elements in the energy region $\varepsilon\approx\varepsilon'$ as

$$\begin{aligned}D_{kl;k'l'}(r)=&-\frac{\partial}{\partial\varepsilon}\left\{\frac{1}{(\varepsilon-\varepsilon')}\left[Z S^{-2}_{kl;k'l'}(r)+X_{kl;k'l'}(r)\right]\right\}\\&+\frac{1}{\varepsilon-\varepsilon'}\left\{\frac{\partial}{\partial\varepsilon}\left[Z S^{-2}_{kl;k'l'}(r)+X_{kl;k'l'}(r)\right]\right.\\&\left.+r W_{kl;k'l'}(r)\right\}.\end{aligned}\tag{47}$$

This form is particularly useful since, as it was shown above, the quantities inside the brackets of the first term and inside the curly brackets of the second term become independent of r in the limit $\varepsilon\to\varepsilon'$, and thus cancel the corresponding terms of the $D_{kl;k'l'}(r_c)$ component. This is especially convenient when the dipole matrix element of Eq. (45) appears as the integrand of matrix element (3). Then, in the energy region $\varepsilon\approx\varepsilon'$, it is beneficial to express its two components according to Eq. (47) in order to avoid the square of the energy difference in the denominator (see below).

B. The case of the EDA and comparison with the results of Refs. [19,20]

In this case, we take the limit $r\to\infty$. Therefore, we may omit terms containing $k+k'$ in the trigonometric functions because, considered as the kernel of an integral operator, their contribution is negligible. Taking into account (27) and (36) and Appendix B, we rewrite (47) in terms of wave numbers in the neighborhood $k \approx k'$ as

$$\begin{aligned}\lim_{r\to\infty} D_{kl;k'l\pm1}(r) = {} & \frac{\partial}{k\partial k}\left\{\frac{1}{\pi}\lim_{R\to\infty}\frac{\cos[(k-k')R+\delta_{kl}-\delta_{k'l\pm1}]}{k-k'}\right\} + \frac{1}{\pi k}\frac{\partial\delta_{kl}}{\partial k}\lim_{R\to\infty}\frac{\sin[(k-k')R+\delta_{kl}-\delta_{k'l\pm1}]}{k-k'} \\ & -\frac{1}{k^2}\left(\frac{1}{2}\mp l_>\right)\frac{1}{\pi}\lim_{R\to\infty}\frac{\cos[(k-k')R+\delta_{kl}-\delta_{k'l\pm1}]}{k-k'} - \frac{Z}{2k^2}\frac{\operatorname{sgn}(k-k')}{k-k'}\cos(\delta_{kl}-\delta_{kl\pm1}) \\ & + \frac{Z}{\pi k^2}\frac{[\gamma+\ln|k-k'|]}{k-k'}\sin(\delta_{kl}-\delta_{kl\pm1}). \qquad (48)\end{aligned}$$

In Appendix C, we show how the term containing the derivative together with a similar term arising from $D_{kl;k'l\pm1}(r_c)$ can be manipulated in a practical way.

We recall the relations

$$\delta(k-k') = \frac{1}{\pi}\lim_{R\to\infty}\frac{\sin(k-k')R}{(k-k')} \quad \text{and} \quad \mathrm{P}\frac{1}{(k-k')} = \lim_{R\to\infty}\frac{1-\cos(k-k')R}{(k-k')}.$$

Consequently, we can rewrite Eq. (48) as

$$\begin{aligned}\lim_{r\to\infty} D_{kl;k'l\pm1}(r) = {} & \frac{\partial}{k\partial k}\left\{\frac{1}{\pi}\cos\left(\delta_{k'l}-\delta_{k'l\pm1}\right)\lim_{R\to\infty}\frac{\cos(k-k')R}{(k-k')} - \sin\left(\delta_{k'l}-\delta_{k'l\pm1}\right)\delta(k-k')\right\} \\ & + \left\{\frac{\partial\delta_{kl}}{\partial k}\cos(\delta_{kl}-\delta_{kl\pm1}) + \left(\frac{1}{2}\mp l_>\right)\frac{1}{k}\sin(\delta_{kl}-\delta_{kl\pm1})\right\}\delta(k-k') \\ & + \left\{\frac{\partial\delta_{kl}}{\partial k}\sin(\delta_{kl}-\delta_{kl\pm1}) - \left(\frac{1}{2}\mp l_>\right)\frac{1}{k}\cos(\delta_{kl}-\delta_{kl\pm1})\right\}\frac{1}{\pi}\lim_{R\to\infty}\frac{\cos(k-k')R}{(k-k')} \\ & - \frac{Z}{2k^2}\frac{\operatorname{sgn}(k-k')}{k-k'}\cos(\delta_{kl}-\delta_{kl\pm1}) + \frac{Z}{\pi k^2}\frac{\gamma+\ln|k-k'|}{k-k'}\sin(\delta_{kl}-\delta_{kl\pm1}). \qquad (49)\end{aligned}$$

The last line contains singular terms resulting from the energy derivative of $S^{-2}_{kl;k'l'}(r)$ that cancel similar terms in $S^{-2}_{kl;k'l'}(r_c)$. Note that the quantities multiplying $\lim_{R\to\infty}\frac{\cos(k-k')R}{(k-k')}$ in the above expression equal the value of the corresponding quantities in $D_{kl;k'l'}(r_c)$ for $k = k'$. Therefore, they simply give rise to principal value integrals. The same is true for the last two terms in Eq. (49).

In the hydrogenic case, we can put $r_c = 0$, in which case, since $y_{kl} \approx r^{l+1}$ for small values of r, the component $D_{kl;k'l'}(r_c)$ becomes simply

$$D_{kl;k'l'}(0) \equiv \frac{Z\,S^{-2}_{kl;k'l'}(0)}{(\varepsilon-\varepsilon')^2}, \qquad (50)$$

while the additional phase shifts due to the core orbitals are zero.

Then, it can be checked that the expression (49) gives identical results (except for a term that depends on the normalization), with the expression derived by Véniard and Piraux [20], who used the analytic properties of the confluent hypergeometric functions building on an initial derivation by Madajczyk and Trippenbach [19]. To facilitate the comparison we note that in the hydrogenic case, the $\frac{Z}{k^2}$ term resulting from $\frac{\partial\delta_{kl}}{\partial k}$ in Eq. (49) [see expression (37)] cancels the $\mp\frac{l_>}{k}$ term in the factor of $\lim_{R\to\infty}\frac{\cos(k-k')R}{(k-k')}$ while the two add up in the factor of the δ function to give $\frac{1}{k}\sqrt{l_>^2+\frac{Z^2}{k^2}}\,\delta(k-k')$. Such a δ function results in the aforementioned derivations from a term resembling the orthogonality relation.

In conclusion, formula (49), which was derived for the general case of arbitrary polyelectronic atomic states, indeed reduces to results previously obtained for the particular case of hydrogen [19,20], where the mathematical analysis is based on the use of the known eigenfunctions. In practice, the $D_{kl;k'l'}(r_c)$ component can be obtained to a very good approximation from fixed-core Hartree-Fock wave functions.

C. The case of the simplified form of the full dipole, Eq. (9)

In this case, we put $r = r_0$, a large enough radius that depends on the wavelength of the radiation. Although r_0 is finite, $\lim_{k\to k'} D_{kl;k'l'}$ is independent of its value and the results of the previous section still apply.

According to Eq. (12), for distances greater than r_0 the matrix element becomes $r_0 S_{kl;k'l'}(r_0)$. In Appendix A we prove that,

$$\begin{aligned}S_{kl;k'l'}(r_0) = {} & \cos(\delta_{kl}-\delta_{kl'})\delta(\varepsilon-\varepsilon') \\ & + \mathrm{P}\frac{1}{\varepsilon-\varepsilon'}\big[C_{ll'}S^{-2}_{kl;k'l'}(r_0) + W_{kl;k'l'}(r_0)\big]. \qquad (51)\end{aligned}$$

Although D_{SF}, being finite at infinity, behaves better than the pure length form of the EDA, the resulting matrix elements are complicated. Specifically, the $D_{kl;k'l'}(r_0)$ component at low energies may be as complicated as $D_{kl;k'l'}(r_c)$, because the wave functions have not attained their asymptotic forms. In this case, a more accurate form than the asymptotic one is required, and this is the WKB form (see Appendix D):

$$y_{kl} = \sqrt{\frac{2}{\pi}} \frac{1}{\sqrt{\zeta_{kl}(r)}} \sin \varphi_{kl}(r). \quad (52)$$

In the limit of large distances, for $k > 0$,

$$\lim_{r\to\infty} \zeta_{kl}(r) = k \quad \text{and} \quad \lim_{r\to\infty} \varphi_{kl}(r) = kr + \frac{Z}{k} \ln r + \delta_{kl}. \quad (53)$$

The WKB wave function is accurate for energies down to $\varepsilon = 0$ for reasonably small values of r (beyond the inner turning point). A further advantage of this form relies in the fact that it allows the explicit computational treatment of the oscillatory part of the matrix elements. As it is shown in Appendix D, the expressions for X and W are written in terms of trigonometric functions of sums and differences of phases multiplied by amplitudes that vary smoothly with the energies. These expressions can now be treated as integrands in the spirit of Filon's integration, where one fits the smooth parts, here phases and amplitudes, by low-order polynomials, and then performs the integrals of the rapidly oscillating parts analytically. The $S^{-2}_{kl;k'l'}$ integrals containing WKB functions are calculated by a method described by Sil, Crees, and Seaton [33], which involves deformation of the integration contours into the complex plane.

IV. SYNOPSIS AND CONCLUDING REMARKS

In the Introduction of this paper, we outlined arguments having to do with the nonperturbative solution of the time-dependent many-electron problem (TDMEP) that characterizes a variety of multiphoton processes which can be generated when intense radiation pulses interact with states of polyelectronic atoms or molecules. In such processes, it is crucial for theory and computation to be able to provide reliable information as to the quantitative aspects of the role played by the multichannel (in general) continuous spectrum, without or with resonance states. Our proposed theoretical framework for the efficient and transparent treatment of such TDMEPs has been the implementation of the state-specific expansion approach (SSEA) [1,2].

A thorny issue which emerges in this context is the rigorous and practical calculation of matrix elements of the atom (molecule)-field interaction corresponding to both on- and off-resonance couplings. In this paper, we have presented a method of calculating free-free (f-f) transition matrix elements in N-electron atoms of an operator, $D_{SF}(r)$ of Eq. (9), which is a very good approximation to the full electric operator of the multipolar Hamiltonian, Eq. (5). These matrix elements can be used in state-specific treatments of the continuous spectrum within time-dependent as well as time-independent theoretical frameworks. (The basics of the analysis also hold for high-n Rydberg-free transition matrix elements.)

We point out that, as mentioned in Sec. I D, a study of the solution of the TDSE using the full multipolar Hamiltonian was carried out in Ref. [32] for a prototypical problem involving off-resonance couplings of high-n Rydberg states.

The use of $D_{SF}(r)$, which represents the dipole coupling part of the full operator, can obviously reduce the magnitude of complexity of problems where the continuous spectrum acquires physical and computational significance. The need for computing field-atom coupling matrix elements at a level of theory that is beyond the electric dipole approximation (EDA) and employs $D_{SF}(r)$ is linked to the fact that, for problems where the field is strong, even if the wavelength is not in the x-ray region, off-resonance matrix elements involving Rydberg and, mainly, scattering states, may contribute significantly to the observed physical quantity. In N-electron systems, the wave functions of such states must be computed numerically, with the correct asymptotic boundary conditions. In that case, they either extend to very large distances (Rydberg) or they are unbound with sinusoidal behavior (scattering). Therefore, there is no *a priori* justification for the use of the EDA in computing the Rydberg-free and (mainly) the free-free coupling matrix elements.

$D_{SF}(r)$ is depicted in Fig. 2, where it is compared to the exact behavior of the full electric operator. Its fundamental characteristic is that it is equal to the usual length operator of the EDA up to a radial distance r_0, which is predicted by theory via the simple formula (10). From then on, it stops increasing and becomes finite by remaining equal to the r_0.

As regards the mathematical theory and its practical implementation regarding the computation of free-free matrix elements, we point to our result of Eq. (45). This matrix element consists of two terms of the form (46), which become independent of r at $\varepsilon = \varepsilon'$, while the same is true of their derivatives. By rearranging Eq. (46), we obtain Eq. (47), which is a convenient expression in the vicinity of the singular point, since it renders the cancellation between the two terms obvious. Furthermore, by reducing the second-order pole to a derivative of the first-order pole, expression (47) facilitates its use as an integrand in matrix elements of the type of Eq. (3).

Depending on the operator one considers, the outer radius is either taken to infinity [Eqs. (48) and (49)], or is given the value r_0 specified by the wavelength of the radiation [Eq. (9)]. In the latter case, a different formula, depending on the overlap instead of the dipole, is used in the region from r_0 to infinity (Appendix A).

We note that the herein derived expression for the diagonal singularity of the length form of the standard EDA corrects previously published formulas [7,10,11], by incorporating the part at infinity which provides the correct behavior at $\varepsilon = \varepsilon'$.

The results of this work can be of use in a variety of problems of current and future interest in the broad subject of multiphoton processes induced by strong electromagnetic fields, where the correct accounting of f-f matrix elements may not be neglected *a priori*. For example, we point to a recent publication by Sato *et al.* [34], who measured the absolute values of the two-photon ionization cross section of helium at four different wavelengths in the extreme ultraviolet regime (53.4–61.4 nm) for pulses of intense free-electron radiation of duration of 300 fs. The comparison of the experimental values with all previous theoretical results shows significant discrepancies (Table 2 and Fig. 3 of Ref. [34]), and this fact suggests the additional exploration of this prototypical system, where the high-order, nonlinear contributions of the continuous spectrum are taken into account rigorously. It is our intention to implement the SSEA using the formulas for the matrix elements of the operator $D_{SF}(r)$ reported here in order to solve the TDSE nonperturbatively and contribute useful information towards the solution of this open problem [34].

Finally, we point out that the analysis and computational methodology presented here should be applicable to the treatment of relativistic atoms as well as to diatomic molecules, where energy-normalized scattering wave functions in a fixed $(N-1)$ electron core can also be computed numerically. In this framework, ground or excited bound electronic structures of diatomic molecules can be calculated via numerical methods in spheroidal coordinates, including electron correlation, e.g., Ref. [35]. Hence, it would be possible to compute numerically the matrix elements up to the radius r_c in spheroidal coordinates, and then apply the present formalism for the outer region in terms of an effective atomic potential by matching the wave functions appropriately.

APPENDIX A: OVERLAP OF POSITIVE-ENERGY WAVE FUNCTIONS

For values of the radial distance r larger than r_c, for which the effect of the core orbitals is negligible, any one-electron atomic Hamiltonian assumes the form of a hydrogenic one, so that, for $r > r_c$,

$$h y_{kl} \equiv \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] y_{kl} = \varepsilon y_{kl}. \tag{A1}$$

We are interested in the region of the continuous energies $\varepsilon = k^2/2$, and we wish to calculate the overlap of two wave functions corresponding to different values of the angular momentum l,

$$S_{kl;k'l'}(r_0) \equiv \int_{r_0}^{\infty} dr\, y_{kl}\, y_{k'l'}, \tag{A2}$$

for $r_0 > r_c$. From Eq. (A1) we obtain

$$(\varepsilon - \varepsilon') \int_{r_0}^{\infty} dr\, y_{kl}\, y_{k'l'} = \int_{r_0}^{\infty} dr (y_{k'l'} h y_{kl} - y_{kl} h' y_{k'l'}). \tag{A3}$$

Taking the explicit expression of the Hamiltonian into account, we write

$$(\varepsilon - \varepsilon') S_{kl;k'l'}(r_0) = -\frac{1}{2}\left[y_{k'l'} \frac{d}{dr} y_{kl} - y_{kl} \frac{d}{dr} y_{k'l'} \right]_{r_0}^{\infty} + C_{ll'} \int_{r_0}^{\infty} dr\, y_{k'l'} \frac{1}{r^2} y_{kl}, \tag{A4}$$

where

$$C_{ll'} = \tfrac{1}{2} l(l+1) - \tfrac{1}{2} l'(l'+1). \tag{A5}$$

In the spirit of Eq. (A2), let us define

$$S^{-2}_{kl;k'l'}(r_0) \equiv \int_{r_0}^{\infty} dr \frac{1}{r^2} y_{k'l'}\, y_{kl} \tag{A6}$$

and also put

$$W_{kl;k'l'}(r) \equiv \frac{1}{2}\left[y_{k'l'} \frac{d}{dr} y_{kl} - y_{kl} \frac{d}{dr} y_{k'l'} \right]. \tag{A7}$$

Then, Eq. (A4) is written as

$$(\varepsilon - \varepsilon') S_{kl;k'l'}(r_0) = -\lim_{r\to\infty} W_{kl;k'l'}(r) + W_{kl;k'l'}(r_0) + C_{ll'} S^{-2}_{kl;k'l'}(r_0). \tag{A8}$$

For $r \to \infty$, the asymptotic form of y is

$$y_{kl} = \sqrt{\frac{2}{\pi k}} \sin\left(kr + \frac{Z}{k} \ln r + \delta_{kl} \right), \tag{A9}$$

where

$$\delta_{kl} = \sigma_l(k) + \frac{Z}{k} \ln 2k - l\pi/2 + \delta^{v}_{kl}. \tag{A10}$$

$\sigma_l(k)$ is the Coulomb phase shift and δ^{v}_{kl} is the additional phase shift caused by the nonhydrogenic terms. Therefore,

$$\lim_{r\to\infty} W_{kl;k'l}(r) = -\frac{k+k'}{2\pi\sqrt{kk'}} \lim_{R\to\infty} \sin[(k-k')R + \delta_{kl} - \delta_{k'l'}] + \frac{k-k'}{2\pi\sqrt{kk'}} \lim_{R\to\infty} \sin[(k+k')R + \delta_{kl} + \delta_{k'l'}], \tag{A11}$$

where the substitution $R = r - \frac{Z}{kk'} \ln r$ has been applied. Regarded as the kernel of an integral operator, the second term has no contribution, and can be omitted. Note that for $k = k'$, $\lim_{r\to\infty} W_{kl;kl}(r) = -\frac{1}{\pi} \sin(\delta_{kl} - \delta_{kl'})$.

We now discuss two cases. (i) We shall examine Eq. (A8) initially for the case of a pure hydrogenic Hamiltonian, for which we can put $r_0 = 0$. In the case $l = l'$, this expression is used to define the energy-normalized wave functions. Because $C_{ll'} = 0$, $y_{kl}(0) = 0$, and $W_{kl;k'l'}(0) = 0$, Eq. (A8) gives

$$(\varepsilon - \varepsilon') S_{kl;k'l'} = \frac{k+k'}{2\pi\sqrt{kk'}} \lim_{R\to\infty} \sin[(k-k')R]. \tag{A12}$$

Using the well-known expression for the δ function,

$$\delta(k-k') = \frac{1}{\pi} \lim_{R\to\infty} \frac{\sin(k-k')R}{k-k'}, \tag{A13}$$

we finally get

$$S_{kl;k'l} = \frac{1}{k}\delta(k-k') \equiv \delta(\varepsilon - \varepsilon'). \tag{A14}$$

In the case where $l \neq l'$, the corresponding expression is slightly more complicated:

$$(\varepsilon - \varepsilon') S_{kl;k'l'} = C_{ll'} S^{-2}_{kl;k'l'} + \frac{k+k'}{2\pi\sqrt{kk'}} \lim_{R\to\infty} \sin[(k-k')R + \delta_{kl} - \delta_{k'l'}]. \tag{A15}$$

Note that for $k = k'$ the above expression reduces to

$$C_{ll'} S^{-2}_{kl;kl'} = -\frac{1}{\pi} \sin(\delta_{kl} - \delta_{kl'}). \tag{A16}$$

Now, for $k \neq k'$, Eq. (A15) takes the form

$$S_{kl;k'l'} = \frac{C_{ll'}}{\varepsilon - \varepsilon'} S^{-2}_{kl;k'l'} + \frac{1}{\pi\sqrt{kk'}} \lim_{R\to\infty} \frac{\sin(k-k')R}{(k-k')} \times \cos(\delta_{kl} - \delta_{k'l'}) + \frac{1}{\pi\sqrt{kk'}} \times \lim_{R\to\infty} \frac{\cos(k-k')R}{(k-k')} \sin(\delta_{kl} - \delta_{k'l'}), \tag{A17}$$

which gives

$$\begin{aligned} S_{kl;k'l'} = {} & \frac{1}{k}\delta(k-k')\cos(\delta_{kl}-\delta_{kl'}) + \frac{C_{ll'}}{\varepsilon-\varepsilon'}S^{-2}_{kl;k'l'} \\ & + \frac{1}{\pi\sqrt{kk'}}\lim_{R\to\infty}\frac{\cos(k-k')R}{(k-k')}\sin(\delta_{kl}-\delta_{k'l'}). \end{aligned} \tag{A18}$$

As a kernel, the last term has no contribution, except for the value $k = k'$, where, due to Eq. (A16), it exactly cancels the second term. Specifically, one of the expressions for the principal value of $(k-k')^{-1}$ is

$$\mathrm{P}\frac{1}{(k-k')} = \lim_{R\to\infty}\frac{1-\cos(k-k')R}{(k-k')}.$$

Therefore, we can write (A18) as

$$S_{kl;k'l'} = \delta(\varepsilon-\varepsilon')\cos(\delta_{kl}-\delta_{kl'}) + \mathrm{P}\frac{C_{ll'}}{\varepsilon-\varepsilon'}S^{-2}_{kl;k'l'}, \tag{A19}$$

where P stands for principal value integration.

(ii) We shall examine the general case of a Hamiltonian which becomes hydrogenic asymptotically. Now, r_0 has a finite value and the quantity $W_{kl;k'l'}(r_0)$ in Eq. (A8) is different from zero. As a consequence, this term is added to $C_{ll'}S^{-2}_{kl;k'l'}(r_0)$ in Eqs. (A16)–(A19). Specifically, Eq. (A16) becomes

$$C_{ll'}S^{-2}_{kl;kl'}(r_0) + W_{kl;kl'}(r_0) = -\frac{1}{\pi}\sin(\delta_{kl}-\delta_{kl'}), \tag{A20}$$

where the additional phase shifts due to the core are included in δ_{kl}. The final expression is

$$\begin{aligned} S_{kl;k'l'}(r_0) = {} & \cos(\delta_{kl}-\delta_{kl'})\delta(\varepsilon-\varepsilon') + \mathrm{P}\frac{1}{\varepsilon-\varepsilon'} \\ & \times\left[C_{ll'}S^{-2}_{kl;k'l'}(r_0) + W_{kl;k'l'}(r_0)\right]. \end{aligned} \tag{A21}$$

APPENDIX B: ACCELERATION INTEGRAL OF POSITIVE-ENERGY WAVE FUNCTIONS

We are interested in the region of the continuous energies $\varepsilon = k^2/2$ and we wish to calculate the acceleration integral of two wave functions corresponding to different values of the angular momentum l:

$$S^{-2}_{kl;k'l'}(r) \equiv \int_r^\infty dr'\frac{1}{r'^2}y_{k'l'}y_{kl}. \tag{B1}$$

For energies not at the ionization threshold and for $r\to\infty$, the asymptotic form of y is

$$y_{kl} = \sqrt{\frac{2}{\pi k}}\sin\left(kr + \frac{Z}{k}\ln r + \delta_{kl}\right),$$

where

$$\delta_{kl} = \sigma_l(k) + \frac{Z}{k}\ln 2k - l\pi/2 + \delta^v_{kl}.$$

$\sigma_l(k)$ is the Coulomb phase shift and δ^v_{kl} is the additional phase shift caused by the nonhydrogenic terms. Using standard trigonometric formulas, (B1) can be written as

$$\begin{aligned} S^{-2}_{kl;k'l'}(r) = {} & \frac{1}{\pi\sqrt{kk'}}\cos(\delta_{kl}-\delta_{k'l'})\int_r^\infty\frac{dr'}{r'^2}\cos(k-k')R \\ & - \frac{1}{\pi\sqrt{kk'}}\sin(\delta_{kl}-\delta_{k'l'})\int_r^\infty\frac{dr'}{r'^2}\sin(k-k')R \\ & - \frac{1}{\pi\sqrt{kk'}}\cos(\delta_{kl}+\delta_{k'l'})\int_r^\infty\frac{dr'}{r'^2}\cos(k+k')R \\ & + \frac{1}{\pi\sqrt{kk'}}\sin(\delta_{kl}+\delta_{k'l'})\int_r^\infty\frac{dr'}{r'^2}\sin(k+k')R, \end{aligned} \tag{B2}$$

where

$$R = r' - \frac{Z}{kk'}\ln r'.$$

For sufficiently large values of r, the logarithmic term can be neglected in the evaluation of the above integrals. Performing an initial integration by parts and using the definition of the sine and cosine integrals

$$\mathrm{sgn}(a)\mathrm{si}(|a|\,r) = -\int_r^\infty dr'\frac{\sin(ar')}{r'} \tag{B3}$$

and

$$\mathrm{ci}(|a|\,r) = -\int_r^\infty dr'\frac{\cos(ar')}{r'}, \tag{B4}$$

where $\mathrm{sgn}(a)$ is the sign of a, we obtain

$$\begin{aligned} S^{-2}_{kl;k'l'}(r) = {} & \frac{1}{\pi\sqrt{kk'}}\cos(\delta_{kl}-\delta_{k'l'})\left[\frac{1}{r}\cos(k-k')r + |k-k'|\mathrm{si}(|k-k'|r)\right] - \frac{1}{\pi\sqrt{kk'}}\sin(\delta_{kl}-\delta_{k'l'}) \\ & \times\left[\frac{1}{r}\sin(k-k')r - (k-k')\mathrm{ci}(|k-k'|r)\right] - \frac{1}{\pi\sqrt{kk'}}\cos(\delta_{kl}+\delta_{k'l'})\left[\frac{1}{r}\cos(k+k')r + (k+k')\mathrm{si}[(k+k')r]\right] \\ & + \frac{1}{\pi\sqrt{kk'}}\sin(\delta_{kl}+\delta_{k'l'})\left[\frac{1}{r}\sin(k+k')r - (k+k')\mathrm{ci}[(k+k')r]\right]. \end{aligned} \tag{B5}$$

It is of interest to investigate the behavior of these functions for large values of their argument. To this purpose, we express them in terms of a pair of auxiliary functions f and g:

$$\mathrm{si}(z) = -f(z)\cos z - g(z)\sin(z), \tag{B6}$$

$$\mathrm{ci}(z) = f(z)\sin(z) - g(z)\cos(z), \tag{B7}$$

which behave asymptotically as

$$f(z)\sim\frac{1}{z}\quad\text{and}\quad g(z)\sim\frac{1}{z^2}.$$

Then, for $|k-k'|r \gg 1$, (B5) becomes

$$\begin{aligned} S^{-2}_{kl;k'l'}(r) \sim{}& \frac{\cos(\delta_{kl}-\delta_{k'l'})}{\pi\sqrt{kk'}(k-k')r^2}\sin(k-k')r \\ &+ \frac{\sin(\delta_{kl}-\delta_{k'l'})}{\pi\sqrt{kk'}(k-k')r^2}\cos(k-k')r \\ &- \frac{\cos(\delta_{kl}+\delta_{k'l'})}{\pi\sqrt{kk'}(k+k')r^2}\sin(k+k')r \\ &- \frac{\sin(\delta_{kl}+\delta_{k'l'})}{\pi\sqrt{kk'}(k+k')r^2}\cos(k+k')r. \end{aligned} \tag{B8}$$

Note that, due to the cancellations in Eq. (B5), r appears squared in the denominator.

On the other hand, for small values of the argument the sine and cosine integrals behave as

$$\mathrm{si}(z) \approx -\frac{\pi}{2} + z, \tag{B9}$$

$$\mathrm{ci}(z) \approx \gamma + \ln(z) - \frac{1}{4}z^2, \tag{B10}$$

where γ is the Euler constant. As a consequence, the first two terms in Eq. (B5) exhibit singular behavior in their derivative in the limit $k' \to k$.

Specifically, the derivative of the second term has a logarithmic singularity in this limit, while that of the first has a step discontinuity at $k' = k$. To see this, we examine the expression (B5) for large values of r_0 and small values of $\left|k-k'\right|$, such that $\left|k-k'\right| r \ll 1$. Using (B9) and (B10) we get

$$\begin{aligned} S^{-2}_{kl;k'l'}(r) \approx{}& \frac{1}{\pi\sqrt{kk'}}\cos(\delta_{kl}-\delta_{k'l'})\left[\frac{1}{r}-\frac{\pi}{2}|k-k'|\right] \\ &- \frac{1}{\pi\sqrt{kk'}}\sin(\delta_{kl}-\delta_{k'l'})(k-k') \\ &\times [1-(\gamma+\ln|k-k'|+\ln r)], \end{aligned} \tag{B11}$$

Therefore,

$$S^{-2}_{kl;kl'}(r) \sim \frac{\cos(\delta_{kl}-\delta_{kl'})}{\pi k r} + O\left(\frac{1}{r^2}\right) \to 0, \tag{B12}$$

while

$$\begin{aligned} &\lim_{k\to k'} \frac{\partial}{k\partial k} S^{-2}_{kl;k'l'}(r) \\ &\sim \frac{\delta'_{kl}}{2k}|k-k'|\sin(\delta_{kl}-\delta_{k'l'}) - (k-k')\frac{\delta'_{kl}}{\pi k}\cos(\delta_{kl}-\delta_{k'l'}) \\ &\times [1-(\gamma+\ln|k-k'|+\ln r)] \\ &- \frac{1}{2k^2}\cos(\delta_{kl}-\delta_{k'l'})\mathrm{sgn}(k-k') \\ &+ \frac{1}{\pi k^2}\sin(\delta_{kl}-\delta_{k'l'})[\gamma+\ln|k-k'|+\ln r]. \end{aligned} \tag{B13}$$

Recall that the sign function can be written in terms of the step function as $\mathrm{sgn}(x) = 2St(x) - 1$.

APPENDIX C: INTEGRALS INVOLVING THE DERIVATIVE OF INTEGRANDS

We want to examine integrals that contain integrands in the form of derivatives as those in Eq. (48). Together with a similar term arising from the dipole component at the radius r_c, which here we symbolize as $F_{kk'}$, we obtain

$$I = \int_{k'-\delta k}^{k'+dk} dk\, C_k \frac{\partial}{\partial k}\left\{\frac{F_{kk'}}{k-k'} - \frac{1}{\pi}\frac{\cos[(k-k')R+\delta_{kk'}]}{k-k'}\right\}, \tag{C1}$$

where

$$F_{kk} = \frac{1}{\pi}\cos\delta_{kk}. \tag{C2}$$

We split the integral $I = I_1 + I_2$, where

$$I_1 = \int_{k'-\delta k}^{k'+dk} dk\, C_k \frac{\partial}{\partial k}\left\{\frac{F_{kk'}}{k-k'} - \frac{1}{\pi}\cos\delta_{kk'}\frac{\cos(k-k')R}{k-k'}\right\} \tag{C3}$$

and

$$I_2 = \int_{k'-\delta k}^{k'+dk} dk\, C_k \frac{\partial}{\partial k}\left\{\frac{1}{\pi}\sin\delta_{kk'}\frac{\sin(k-k')R)}{k-k'}\right\}. \tag{C4}$$

For $R \to \infty$, the expression inside the brackets in I_1 gives rise to a principal value integral while the corresponding one in I_2 becomes a δ function. The derivative with respect to k produces second-order quantities whose meaning is made clear upon integrating by parts:

$$\begin{aligned} I_1 ={}& \left\{C_k\frac{F_{kk'}-\pi^{-1}\cos\delta_{kk'}\cos(k-k')R)}{k-k'}\right\}_{k'-\delta k}^{k'+\delta k} \\ &- \int_{k'-\delta k}^{k'+dk} dk\,\frac{\partial C_k}{\partial k}\left\{\frac{F_{kk'}-\pi^{-1}\cos\delta_{kk'}\cos(k-k')R)}{k-k'}\right\}, \end{aligned} \tag{C5}$$

$$\begin{aligned} I_2 ={}& \left\{C_k\frac{1}{\pi}\sin\delta_{kk'}\frac{\sin(k-k')R)}{k-k'}\right\}_{k'-\delta k}^{k'+\delta k} \\ &- \int_{k'-\delta k}^{k'+dk} dk\,\frac{\partial C_k}{\partial k}\left\{\frac{1}{\pi}\sin\delta_{kk'}\frac{\sin(k-k')R)}{k-k'}\right\}. \end{aligned} \tag{C6}$$

As integrands, the first term in each of the above expressions gives a zero contribution for $R \to \infty$. The remaining integral in I_1 can be evaluated numerically by fitting the functions $\frac{\partial C_k}{\partial k}F_{kk'}$, $\frac{\partial C_k}{\partial k}\cos\delta_{kk'}$, and $\frac{\partial C_k}{\partial k}\sin\delta_{kk'}$ to polynomials. For practical purposes, a linear fitting usually seems adequate. The evaluation of I_2 is straightforward since it contains a δ function.

APPENDIX D: POSITIVE-ENERGY WKB WAVE FUNCTIONS

We follow the development of Seaton and Peach [36]. Consider the solution of the hydrogenic Schrödinger equation,

$$\left[\frac{d^2}{dr^2} + w(r)\right] y_{kl}(r) = 0, \tag{D1}$$

where

$$w(r) = k^2 + \frac{2Z}{r} - \frac{l(l+1)}{r^2}. \tag{D2}$$

For r such that $w > 0$, i.e., beyond the inner turning point, the solution of Eq. (D1) is

$$y = \sqrt{\frac{2}{\pi}} \frac{1}{\sqrt{\zeta(r)}} \sin\varphi(r), \tag{D3}$$

with the constraint

$$\zeta(r) = \frac{\partial}{\partial r}\varphi(r). \tag{D4}$$

In order that Eq. (D1) is satisfied,

$$\zeta^2 = w + \zeta^{1/2}\frac{d^2}{dr^2}\zeta^{-1/2}. \tag{D5}$$

Equation (D5) is solved by iteration.

The phase is defined so as to obey, for $r \to \infty$,

$$\varphi \to \varphi_\infty \equiv kr + \frac{Z}{k}\ln(2kr) - l\frac{\pi}{2} + \sigma_l, \tag{D6}$$

The Coulomb phase shift

$$\sigma_l = \arg\Gamma\left(l + 1 - i\frac{Z}{k}\right) \tag{D7}$$

is defined in terms of the Γ function. Choosing the zero-order solution of Eq. (D5), one has

$$\zeta_0 \equiv \sqrt{w} = \sqrt{k^2 + \frac{2Z}{r} - \frac{l(l+1)}{r^2}} \tag{D8}$$

and

$$\varphi_0 \equiv \int \sqrt{w}dr + \text{const}, \tag{D9}$$

where the constant is such that the limit (D6) is satisfied. Then, as Seaton and Peach [36] have shown,

$$\begin{aligned}\phi_0(r) = {}& \zeta r + \eta\ln\left(1 + \frac{k+\zeta}{\eta}r\right)\\ &+ \sqrt{l(l+1)}\cos^{-1}\left[\frac{1 + \frac{l(l+1)}{\eta Zr}(\zeta r - \eta)}{1 + \frac{l(l+1)}{\eta^2}}\right]\\ &+ \left[\sigma_l(\eta) - \eta + \eta\ln\eta - l\frac{\pi}{2}\right],\end{aligned} \tag{D10}$$

where $\eta = \frac{Z}{k}$.

The expression inside the last brackets is finite for $k \to 0$ and the same is true for the whole expression (D10). Specifically,

$$\begin{aligned}\phi_0(r) = {}& 2\sqrt{2Zr - l(l+1)} + \sqrt{l(l+1)}\\ &\times \cos^{-1}\left(\frac{Zr - l(l+1)}{Zr}\right) - l\pi - \frac{\pi}{4}.\end{aligned} \tag{D10a}$$

We now focus on Eq. (18). Because of the existence of the term $rW_{kl;k'l'}(r)$, it is necessary to take the limit of y for large values of r without discarding terms of the order of $\frac{1}{r}$, as is usually the case in the literature. We start by noting that

$$\zeta \to k + \frac{\eta}{r} + O\left(\frac{1}{r^2}\right). \tag{D11}$$

Then, $\varphi \to \varphi_\infty + \frac{b}{2kr}$, in which case,

$$y = \sqrt{\frac{2}{\pi k}}\left(1 - \frac{a}{r}\right)\sin(\varphi_\infty) + \sqrt{\frac{2}{\pi k}}\frac{b}{r}\cos(\varphi_\infty) + O\left(\frac{1}{r^2}\right), \tag{D12}$$

where

$$a = \frac{Z}{2k^2} \quad \text{and} \quad b = \frac{l(l+1) + (Z/k)^2}{2k}. \tag{D13}$$

For values of the radial distance r larger than r_c, any one-electron Hamiltonian assumes the hydrogenic form. The corresponding WKB solution for $r > r_c$ is given by Eq. (D3) with an additional phase shift δ_{kl}^v added in the limiting form (D6) and the last bracket of Eq. (D10).

Using this result, one can evaluate the expressions X and W of Eqs. (19) and (21), with the wild variation of the matrix elements as a function of the energy made explicit. First we note that the derivative of the wave function (D3) is

$$y' = \sqrt{\frac{2}{\pi}}\frac{\zeta}{\sqrt{\zeta}}[\cos\varphi + g\sin\varphi], \tag{D14}$$

where the function

$$g \equiv -\frac{\zeta'}{2\zeta^2} = \frac{1}{r^2\zeta^3}\left(Z - \frac{l(l+1)}{r}\right) \tag{D15}$$

is of the order of $(\frac{1}{r^2})$ if $k \neq 0$, while for $k = 0$ it is of the order of $(\frac{1}{\sqrt{r}})$. Then

$$y_1y_2 = \frac{1}{\pi\sqrt{\zeta_1\zeta_2}}[\cos(\varphi_1 - \varphi_2) - \cos(\varphi_1 + \varphi_2)], \tag{D16}$$

while

$$\begin{aligned}y_1'y_2' = {}& \frac{\zeta_1\zeta_2}{\pi\sqrt{\zeta_1\zeta_2}}[(1 + g_1g_2)\cos(\varphi_1 - \varphi_2)\\ &+ (1 - g_1g_2)\cos(\varphi_1 + \varphi_2)]\\ &+ \frac{\zeta_1\zeta_2}{\pi\sqrt{\zeta_1\zeta_2}}[(g_1 - g_2)\sin(\varphi_1 - \varphi_2)\\ &+ (g_1 + g_2)\sin(\varphi_1 + \varphi_2)]\end{aligned} \tag{D17}$$

and

$$\begin{aligned}W_{12} \equiv {}& \frac{1}{2}[y_1'y_2 - y_1y_2']\\ = {}& \frac{1}{2\pi\sqrt{\zeta_1\zeta_2}}[-(\zeta_1 + \zeta_2)\sin(\phi_1 - \phi_2)\\ &+ (\zeta_1 - \zeta_2)\sin(\phi_1 + \phi_2)]\\ &+ \frac{1}{2\pi\sqrt{\zeta_1\zeta_2}}[(\zeta_1g_1 - \zeta_2g_2)\cos(\phi_1 - \phi_2)\\ &- (\zeta_1g_1 - \zeta_2g_2)\cos(\phi_1 + \phi_2)].\end{aligned} \tag{D18}$$

According to the definition, Eq. (19) of the main text,

$$\begin{aligned}X_{12} = {}& -\frac{1}{2\pi\sqrt{\zeta_1\zeta_2}}[A_{12}^-\cos(\varphi_1 - \varphi_2) + A_{12}^+\cos(\varphi_1 + \varphi_2)]\\ &- \frac{1}{2\pi\sqrt{\zeta_1\zeta_2}}[B_{12}^-\sin(\varphi_1 - \varphi_2) + B_{12}^+\sin(\varphi_1 + \varphi_2)],\end{aligned} \tag{D19}$$

where

$$A^-_{12} = -\left[\frac{D_{12}}{r^2} - \frac{2Z}{r} - (\varepsilon_1 + \varepsilon_2) - \zeta_1\zeta_2(1 + g_1 g_2) + (\zeta_1 g_1 - \zeta_2 g_2)\frac{C_{12}}{r}\right], \tag{D20a}$$

$$A^+_{12} = \left[\frac{D_{12}}{r^2} - \frac{2Z}{r} - (\varepsilon_1 + \varepsilon_2) + \zeta_1\zeta_2(1 - g_1 g_2) + (\zeta_1 g_1 - \zeta_2 g_2)\frac{C_{12}}{r}\right], \tag{D20b}$$

$$B^-_{12} = \left[\zeta_1\zeta_2(g_1 - g_2) + (\zeta_1 + \zeta_2)\frac{C_{12}}{r}\right], \tag{D20c}$$

$$B^+_{12} = \left[\zeta_1\zeta_2(g_1 + g_2) - (\zeta_1 - \zeta_2)\frac{C_{12}}{r}\right]. \tag{D20d}$$

For the sake of completeness we also give the derivatives with respect to the wave number:

$$\frac{\partial\zeta_0}{\partial k} = \frac{k}{\zeta_0}, \tag{D21a}$$

$$\frac{\partial\varphi_0}{\partial k} = \frac{\zeta_0}{k}r - \frac{Z}{k^2}\ln\left(1 + \frac{k+\zeta_0}{Z}kr\right) + \frac{\partial\sigma_l}{\partial k} - \frac{Z}{k^2}\ln\frac{Z}{k}. \tag{D21b}$$

Again these expressions, due to cancellations, are finite in the limit $k \to 0$.

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