

Long-wavelength approximation in on- and off-resonance transitions

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In view of the possibilities of laser spectroscopy with very short pulses and relatively high frequencies, we examine aspects of the theory of atom-field interactions that are related to violation of the condition of the *long-wavelength approximation* (LWA) according to which $kr \ll 1$, where r is “of the order of atomic dimensions” and k is the magnitude of the wave vector. On- and off-resonance transitions are considered, with kr being larger than unity due to the large extent of the two wave functions involved in the coupling matrix element. The implementation of the analysis uses bound-free transition matrix elements with the $n=50$ and 80 hydrogenic functions as initial states and values of k up to 27 eV, which is sufficient to produce $kr > 1$, thereby rendering the LWA inoperative. In spite of this, it is shown that, for on-resonance transitions, the results from the use of the well-known multipole operators resulting from the LWA [e.g., the *electric dipole approximation* (EDA)] agree with those from the exact expressions derived here from the application of the multipolar Hamiltonian. This numerical agreement is proven analytically. As a test of the kind of convergence of the multipole series expansion for small values of k and large r , it is shown that the lowest-order ratio of electric dipole to quadrupole matrix elements decreases rapidly within 1.0 atomic unit above threshold. Finally, it is 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 $\Delta\ell = \pm 1$.

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I. INTRODUCTION

In two recent publications [1,2], we examined aspects of the problem of atom-field interactions, as regards the choice of the coupling operator and its implications when application is made to nonperturbative problems involving high- n Rydberg states. Let λ be the wavelength of the radiation and $\bar{\lambda}_{nn'}$ the wavelength corresponding to the energy difference between two Rydberg states n and n' . One of the conclusions was that, in situations where off-resonance transitions with $\lambda \ll \bar{\lambda}_{nn'}$ are indirectly participating in the dynamics, the *electric dipole approximation* (EDA), which has been the workhorse of one-photon and multiphoton spectroscopy, is unreliable and in fact must be replaced by the full-interaction operator. In our work, the full-interaction matrix elements were computed and analyzed by implementing the *multipolar Hamiltonian* H_{mp} , which is related to the better-known *minimal coupling Hamiltonian* H_{mc} via a gauge transformation [3–7]. The zeroth-order term of the multipole expansion of H_{mp} is the “length” form of the EDA, $\vec{E}(0) \cdot \vec{r}$. Here $\vec{E}(0)$ is the electric field vector without dependence on position. On the other hand, the zeroth-order term for H_{mc} is the “velocity” form of the EDA, $\vec{A}(0) \cdot \vec{p}$, where $\vec{A}(0)$ is the vector potential without dependence on position. Our choice to work

with H_{mp} aimed at establishing a direct correspondence between the results of the length form of the EDA and the results from the application of the operator of the full interaction. The related argument was that, for problems with hydrogenic degeneracies such as the one treated in [2], the $\vec{E}(0) \cdot \vec{r}$ form makes better computational and physical sense to represent the zeroth-order model than the $\vec{A}(0) \cdot \vec{p}$ form, since for the latter one the coupling matrix elements within the same hydrogenic shell, which are overwhelmingly dominant in the length form, are zero. The formalism was developed in such a way as to allow computations with numerical functions, thereby permitting the treatment of high- n Rydberg states of polyelectronic atoms, regardless of electronic structure and quantum defects. The accuracy of the first part of this work [1] was recently confirmed by Parzynski and Sobczak [8], who performed certain related integrations analytically using hydrogenic functions.

The present paper reports additional analysis and results on the general issue of the possible consequences from the breakdown of the *long-wavelength approximation* (LWA) which is effected when the radiative coupling matrix elements are between extended wave functions, for on- and off-resonance processes.

Specifically, we have examined two issues. The first has to do with the formal analysis of the matrix elements of the multipole expansion for atom-field coupling, and the relevance of the LWA. The second concerns the anticipated reduction of the accuracy of the matrix elements in the low-order expansion of the LWA (dipole and quadrupole terms) for high-lying Rydberg states—say, with $n \approx 50$ —which are

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excited and then coupled either directly, on-resonance, to scattering states, or off-resonance to scattering and Rydberg states, by relatively large photons—say, optical or higher. Such situations are relevant to laser spectroscopy with short pulses which, e.g., engage intermediate states with extended wave functions in the discrete and continuous spectra, or excite wave packets in the Rydberg spectrum. In fact, it is the latter that was investigated in [1,2] (earlier work on this Rydberg wave packet excitation problem is cited in [1,2]).

II. MULTIPOLE EXPANSION AND THE LONG-WAVELENGTH APPROXIMATION

It is textbook knowledge that the expression for the full matter-radiation interaction operator involves the plane-wave term $\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}}$. Here $\hat{\epsilon}$ is the polarization vector and \vec{k} is the propagation vector. Taking propagation to be along the z axis, the exponential can be represented by two expansions with infinite terms. The first is the Taylor series, whose first three terms are

$$\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}} = \hat{\epsilon} \left[1 + i\vec{k}\cdot\vec{r} + \frac{1}{2}(i\vec{k}\cdot\vec{r})^2 + \dots \right], \quad (1)$$

and the second is the expansion over the basis set of the spherical Bessel functions, $j_\ell(kr)$,

$$\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}} = \hat{\epsilon}e^{ikr\cos\theta} = \hat{\epsilon} \left[\sum_{\ell=0}^{\infty} (2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos\theta) \right]. \quad (2)$$

Expansion (2) is the appropriate one for transitions between states of spherical symmetry since it leads directly to the derivation of the selection rules. By expressing $j_\ell(kr)$ in powers of kr [see Eq. (10) below] and the Legendre functions $P_\ell(\cos\theta)$ in powers of $\cos\theta$, expansion (2) is transformed into expansion (1).

In practice, one wants to retain the Legendre polynomials because, as said, they give rise to selection rules reducing the infinite summation to a few terms. This is equivalent to writing the powers of $\cos\theta$ appearing in Eq. (1) in terms of Legendre polynomials. Thus, the form which is relevant in practice is a third expansion:

$$\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}} = \hat{\epsilon} \left[P_0 + (ikr)P_1 + (ikr)^2 \left\{ \frac{1}{3}P_2 + \frac{1}{6}P_0 \right\} + \dots \right]. \quad (1')$$

Equation (1') can also be derived from Eq. (2) by expressing $j_\ell(kr)$ in powers of kr and collecting equal powers of kr .

Although expansions (1) and (1') are formally equal to expansion (2), this is not true if a finite number of terms is considered. Such an equality is achieved only after the LWA is made, which has been the fundamental means of simplification and implementation in the theory, leading to the well-known expressions for the multipole ($E1$, $E2$, $M1$, etc.), transition amplitudes, and probabilities.

However, the above is invalidated when the condition for the LWA, inequality (3) below, is violated. In such a case, it

is the expansion in terms of Bessel functions that must be used, something which is not followed in research involving the theory and computation of radiative transitions.

In the following sections we investigate the degree of possible deviations between the full expression for each term of Eq. (2)—we shall call it the “Bessel function matrix element” (BFME)—and the corresponding Eq. (1') that emerges from the LWA, in cases where the two wave functions of the matrix element are extended, meaning cases where the LWA is of dubious validity (see below).

In other words, suppose one focuses on the second term of the expansion (2). For $\ell=1$, this is

$$i3j_1(kr)P_1(\cos\theta) = i3 \left(\frac{\sin(kr)}{(kr)^2} - \frac{\cos(kr)}{kr} \right) \cos\theta,$$

which is different from the second term of Eq. (1), $ikr\cos\theta$. Also suppose that physical conditions are such that the LWA, as is generally stated [see Eq. (3)], cannot be justified. What is the proper choice for the expansion of $\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}}$? Can the use of expansion (1') be justified and under what conditions? To the best of our knowledge, analysis and quantitative answers to these questions do not exist in the literature. An amendment to this situation is presented below.

III. LWA AND TRANSITIONS INVOLVING EXTENDED WAVE FUNCTIONS

The LWA is usually justified by phrases such as “the radiation wavelength is much larger than the atomic dimensions” and is based on the inequality

$$kr \ll 1, \quad \text{condition for the LWA}, \quad (3)$$

where k is the magnitude of the wave vector, $k=2\pi/\lambda = \omega/c$. The electron coordinate r is taken as the measure of “atomic dimensions.”

When Eq. (3) holds, the first two terms of the expansion (2) reduce to the first two terms of Eq. (1) or (1'), since the first terms of the Taylor series expansion [see Eq. (10)] of $j_0(kr)$ and $j_1(kr)$ are

$$j_0(kr) \approx 1 \quad \text{and} \quad j_1(kr) \approx kr. \quad (4)$$

The zeroth-order model that results from Eq. (2) is the EDA, according to which the vector potential or the fields are independent of the coordinate, while the first-order gives the electric quadrupole term,

$$\hat{\epsilon}e^{i\vec{k}\cdot\vec{r}} \approx \hat{\epsilon}[1 + kr\cos\theta]. \quad (5)$$

Expression (5) coincides with the first two terms of the series (1).

It is evident that the key “physical” quantity in the above is the quantity kr . Its value depends on the magnitude of k or of r , which are independent quantities. Although the heuristic notion of r may be confusing, since the two states entering in the transition matrix element need not have the same “atomic dimension,” practically it refers to the less extended state. The present work has placed its emphasis on the r part—i.e., on coupling matrix elements where both states are extended—rather than on the k part. For highly excited

Rydberg states with $n \gg \ell$, we take the outer classical turning point $r_t \approx 2n^2$ as the most representative quantity for the notion of “atomic dimensions.” For example, for $n=50$, $r_t = 5000$ a.u.

It can also be noted that condition (3) does not say anything about possible differences between on- and off-resonance radiative couplings. This issue is also examined below. We find that the breakdown of the LWA condition has more serious implications for the off-resonance case.

The established wisdom on the relative significance of each of the terms of the LWA expansion, or of their interference, has drawn from the physics of the on-resonance interaction with the electromagnetic field of states whose wave functions are relatively compact, such as the various ground or low-lying states of atoms and molecules. Characteristic examples are the normal spectroscopic transitions of the discrete spectrum, where both wave functions are compact, and the subject of the photoelectric effect, where the initial-state wave function is compact.

For the photoelectric effect, the flexibility as regards the value of kr is large, due to the possible large range of k values. Both partial and total cross sections are measured for different subshells and for a broad spectrum of photon energies, from a few eV to keV. As it is evident from the condition of the LWA, since the normal extent of the initial states is, say, around 1–5 a.u., when k is allowed to increase it eventually causes the breakdown of the EDA, relativistically or nonrelativistically, and, in fact, reduces the validity of the truncation of the series (1) or (2). For example, if the initial state is the $1s$ of hydrogen, then $r_t = 1.058 \text{ \AA}$ and the quantity kr_t becomes unity when the ionizing radiation has $\lambda \approx 6.6 \text{ \AA}$.

Various aspects of the consequence of the k dependence of the photoelectric effect have been studied over the years from the x-ray to the VUV regions, the most recent ones focusing on the results of interference of the dipole with terms of the next two orders on the angular distribution of photoelectrons—e.g., [9–12] and references therein.

It is noted that, when attention is paid to the k part, situations of the possible breakdown of the EDA may also arise for transitions in highly positive ions or for emission of radiation of short wavelength from heavy atoms with holes in the inner shells.

A different source of possible breakdown of condition (3) appears in situations where, even for not too short wavelengths—say, from 8000 \AA down to 800 \AA —the wave functions that get involved in the coupling matrix elements are extended. For example, in hydrogen, for the $n=50$ Rydberg state $r_t = 5000$ a.u. This means that the quantity kr_t is unity for $\lambda \approx 16\,600 \text{ \AA}$. This was the case that was examined in [1,2]. The application involved the computation and analysis of time-dependent laser excitation of angular Rydberg wave packets in highly excited hydrogen, a theme that was first discussed within the EDA by Corless and Stroud [13]. Among other things, it was demonstrated that, because of off-resonance couplings, the EDA loses its validity completely.

As a test of the impact of the use of extended wave functions on the on-resonance matrix elements of the multipole expansion, we considered an *on-resonance* transition from a

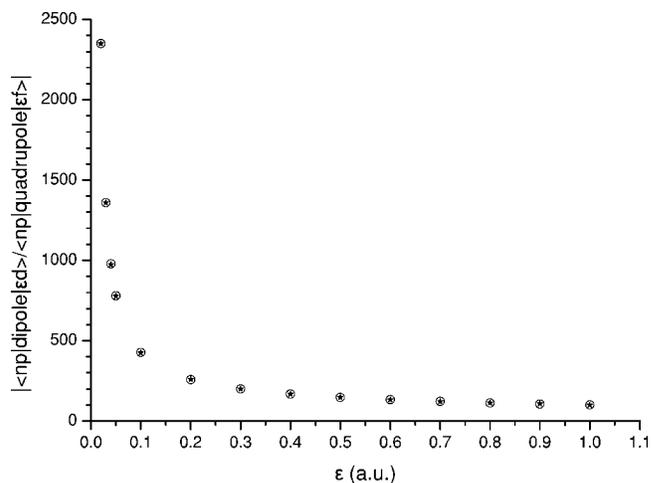


FIG. 1. Ratio of the dipole to quadrupole radial matrix elements as a function of the energy ϵ in a.u. of the scattering electron. The dipole radial matrix elements are calculated between the Rydberg np states and the d states of the continuum. The quadrupole radial matrix elements are calculated between the Rydberg np states and the scattering f states. Open circles correspond to $n=50$ and stars to $n=80$.

Rydberg state to the continuous spectrum, assuming that the condition (3) for the LWA is not valid. For example, such a case may arise in a two-photon ionization of an atom or a positive ion, using UV or VUV photons, where the first step reaches a high-lying Rydberg state or wave packet. *A priori*, there is no reason for the transition matrix element from the Rydberg state to the continuous spectrum to be described accurately by the EDA. For example, consider hydrogen. For $h\nu \approx 13.574 \text{ eV}$ ($\approx 913 \text{ \AA}$), Rydberg states of about $n=50$ can be reached. For $r_t \approx 2n^2 = 5000$ a.u., the product $kr_t = (2\pi/\lambda)r_t$ is about 18, so that condition (3) is violated for the transition from the $n=50$ state to the continuum, with $h\nu \approx 13.574 \text{ eV}$.

The numerical application pertained to the ionization matrix elements of the Rydberg state with n in the range of 50–80, for which, when $h\nu \approx 13.574 \text{ eV}$, the quantity kr is larger than one for the greater extent of the wave function. Calculated values for both the dipole and the quadrupole cases as well as their ratio are shown in Tables I(a) and I(b) for initial Rydberg states $50p$ and $80p$, respectively. It is noteworthy that the ratio does not vary significantly as the high principal quantum number of the initial state changes from 50 to 80.

The results show that the ratio dipole/quadrupole in the energy range 0–27.148 eV above threshold changes rapidly, by almost two orders of magnitude (see Fig. 1). This finding is in harmony with the logic of the relations (1) and (3), since the extent of the initial state is huge and the relative accuracy of the EDA drops fast with respect to the magnitude of k .

IV. “BESSEL FUNCTION MATRIX ELEMENT”: ANALYSIS AND CALCULATIONS

In the theory and calculations that follow, we compare the “Bessel function matrix element” of each term of Eq. (2), as

TABLE I. The dipole and quadrupole radial matrix elements $\langle np | \text{operator} | \varepsilon \ell \rangle$ for various values of the energy ε of the continuum state. The numerical results between $(2\ell+1)F_\ell$ and its small argument limit differ in the sixth decimal place for both the dipole ($\ell=1$) and the quadrupole ($\ell=2$) cases. Also listed is the ratio of the dipole/quadrupole radial matrix elements. (a) Initial state with $n=50$. (b) Initial state with $n=80$.

ε (a.u.)	Dipole or $3F_1$ (a.u.)	Quadrupole or $5F_2$ (a.u.)	10^2 (ratio)
(a)			
0.00	18929.0	-2.53	-74.80
0.02	11.52	4.90×10^{-3}	23.50
0.03	5.94	4.37×10^{-3}	13.60
0.04	3.68	3.76×10^{-3}	9.80
0.05	2.52	3.23×10^{-3}	7.80
0.1	0.74	1.74×10^{-3}	4.27
0.2	0.20	7.76×10^{-4}	2.58
0.3	0.09	4.46×10^{-4}	2.00
0.4	0.05	2.92×10^{-4}	1.68
0.5	0.03	2.06×10^{-4}	1.47
0.6	0.02	1.54×10^{-4}	1.33
0.7	1.14×10^{-2}	1.19×10^{-4}	1.22
0.8	1.08×10^{-2}	0.95×10^{-4}	1.13
0.9	0.83×10^{-2}	0.78×10^{-4}	1.06
1.0	0.65×10^{-2}	0.65×10^{-4}	1.01
(b)			
0.00	43578.0	-4.46	-97.70
0.02	5.75	2.44×10^{-3}	23.50
0.03	2.95	2.16×10^{-3}	13.60
0.04	1.83	1.87×10^{-3}	9.75
0.05	1.25	1.61×10^{-3}	7.78
0.1	0.37	0.85×10^{-3}	4.25
0.2	0.10	0.38×10^{-3}	2.60
0.3	4.41×10^{-2}	2.20×10^{-4}	2.00
0.4	2.42×10^{-2}	1.44×10^{-4}	1.68
0.5	1.51×10^{-2}	1.02×10^{-4}	1.48
0.6	1.01×10^{-2}	0.76×10^{-4}	1.33
0.7	0.72×10^{-2}	0.59×10^{-4}	1.22
0.8	0.53×10^{-2}	0.47×10^{-4}	1.14
0.9	0.41×10^{-2}	0.38×10^{-4}	1.08
1.0	0.32×10^{-2}	0.32×10^{-4}	1.00

determined in the framework of the multipolar Hamiltonian, with the corresponding term of Eq. (1') that is characterized by the same selection rules. There is a one-to-one correspondence between the first two terms of the expansions (1') and (1'') which are the physically interesting cases of dipole and quadrupole transitions. It is shown that condition (3) is sufficient but not necessary for the practical validity of each term of the multipole expansion. In other words, there is good agreement between the two types of matrix elements even when condition (3) is not satisfied—up to a reasonable

degree. The consequences of such comparisons depend on whether the phenomenon involves on- or off-resonance coupling. It is proven analytically and numerically that the off-resonance case is more intriguing, since such couplings are large and may have physical repercussions.

In the formulation of [1], where the *multipolar* Hamiltonian [3–7] was adopted, we showed that the electric field operator can be written in the form

$$O_E = E_0(t) e^{-i\omega t} \sum_{\ell=1}^{\infty} i^{\ell+1} (2\ell+1) F_\ell(r) \Theta(\theta, \phi) + \text{c. c.}, \quad (6)$$

where $E_0(t)$ is the amplitude of the electric field and

$$F_\ell(r) = \frac{1}{k} \int_0^r \frac{1}{r'} j_\ell(kr') dr', \quad (7)$$

$$\Theta(\theta, \phi) = \sqrt{\frac{\ell(\ell+1)}{\pi(2\ell+1)}} (Y_\ell^{-1} - Y_\ell^1), \quad (8)$$

causing transitions with $\Delta m = \pm 1$. Here Y_ℓ^1 is the spherical harmonic. The integral of Eq. (7) has its origin in the electric field operator which is given by $e \sum_j \int_0^1 \vec{r}_j \cdot \vec{E}_T(\lambda \vec{r}_j) d\lambda$ [3–7]. The λ integration allows the writing of expressions that involve an infinite expansion in a compact form. After the expansion of the electric field operator in spherical waves, this integral is reexpressed as an integral over the radial variable.

In Eq. (6), for values of $k \rightarrow 0$, only the first term ($\ell=1$) survives. (Here we consider only the electric field.)

The object of the present analysis is the matrix element of O_E , which is evaluated for transitions between hydrogenic wave functions that, here, are computed via the numerical solution of the differential equation that they satisfy. For highly excited Rydberg states as well as for states of the continuous spectrum, this is a fast and accurate method. Furthermore, it is not restricted to purely hydrogenic atoms and ions.

In what follows, the case of continuum-continuum coupling matrix elements is excluded. This is a case where, when stationary energy-normalized scattering states rather than localized wave packets are considered, the LWA is obviously violated. The EDA result is different, quantitatively and qualitatively, from that obtained from the full operator, since the large- r behavior of the EDA operator ($\sim r$), is different from that of $3F_1$ [Eqs. (6) and (7)], which becomes constant [1] and below. Additional information can be deduced from the Appendix.

For the transitions under investigation, we expected that the results produced by the multipole expansion terms within the LWA would be inadequate, for reasons that are more fundamental than the heuristic kr argument. These reasons have to do with the large- r behavior of F_ℓ [1]. It was shown in [1] that a simple model operator for F_1 ($\ell=1$),

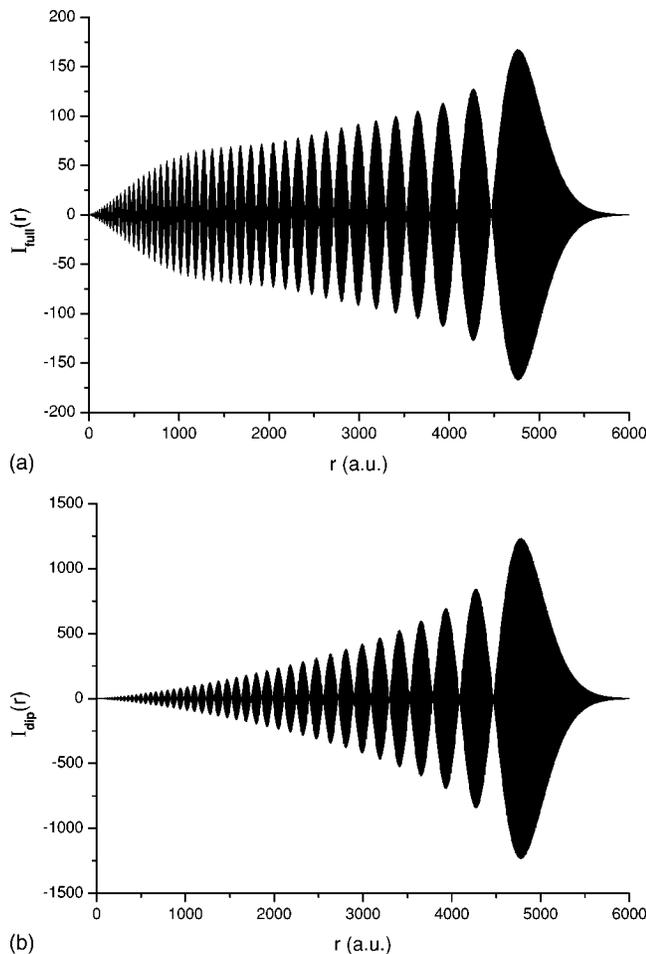


FIG. 2. (a) Cumulative integral $I_{\text{full}}(r) = \int_0^r y_{50p}(x) 3F_1(x) y_{\varepsilon d}(x) dx$, photoelectron energy $\varepsilon = 0.5$ a.u. (b) Cumulative integral $I_{\text{dip}}(r) = \int_0^r y_{50p}(x) x y_{\varepsilon d}(x) dx$.

$$3F_1^{\text{model}} = \begin{cases} r, & r \leq r_0, \\ r_0, & r \geq r_0, \end{cases} \quad (9)$$

where $r_0 = 3\pi/4k$, reproduces the main characteristics of $3F_1$ (Fig. 1 of [1]) and shows that, although the two operators are almost identical in the region $kr < 1$, they differ greatly for larger values since the former reaches a constant value while the latter increases beyond limit.

Therefore, in this work it came as a surprise to us that the matrix elements $\langle \text{Rydberg} | \text{operator} | \text{continuum} \rangle$ calculated by employing the operators for dipole or quadrupole interaction and the corresponding BFME (i.e., where no LWA is made) are essentially the same, given the fact that they involve such extended wave functions. Actually, the plot of the cumulative integral of the matrix elements as a function of r , Figs 2(a) and 2(b), shows that, at places, there are differences of an order of magnitude. However, for values of r where the Rydberg function has become zero, the two results differ only in the sixth decimal place. This result cannot be changed by increasing the principal quantum number n of the Rydberg state—i.e., by making it more extended. The same result is true for other values of ℓ .

The very high degree of coincidence of the numerical results between $(2\ell + 1)F_\ell$ and its small-argument limit—i.e., the LWA—even for cases where kr is substantially greater than unity, led us to the hypothesis that it can be explained analytically using hydrogenic functions. Indeed, the proof is as follows.

We focus on the analysis of the structure of the function $F_\ell(r)$, of Eq. (7). The spherical Bessel function is given by the ascending series

$$j_\ell(x) = \frac{x^\ell}{(2\ell + 1)!!} \left(1 - \frac{x^2/2}{1!(2\ell + 3)} + \frac{(x^2/2)^2}{2!(2\ell + 3)(2\ell + 5)} - \dots \right). \quad (10)$$

Note that only even powers exist within the parentheses. Substitution in Eq. (7) gives

$$(2\ell + 1)F_\ell(r) = \frac{k^{\ell-1} r^\ell}{(2\ell - 1)!!} \left(\frac{1}{\ell} - \frac{k^2 r^2}{2(\ell + 2)(2\ell + 3)} + \dots \right). \quad (11)$$

The first term of the above expansion is the ordinary multipole operator while the higher terms represent corrections to it. In order to test their relative importance, we calculate the first correction to the matrix element of the $2'$ pole, for a radiative transition from a bound state y_1 to a state of the continuous spectrum, y_2 . Pertinent derivations are given in the Appendix.

We obtain

$$(2\ell + 1)\langle y_1 | F_\ell(r) | y_2 \rangle = \frac{k^{\ell-1}}{\ell(2\ell - 1)!!} \langle y_1 | r^\ell | y_2 \rangle \times \left(1 - \frac{\ell k^2}{2(\ell + 2)(2\ell + 3)} \frac{\langle y_1 | r^{\ell+2} | y_2 \rangle}{\langle y_1 | r^\ell | y_2 \rangle} + \dots \right). \quad (12)$$

Putting $n = \ell + 2$ in the relation (A14) of the Appendix, an expression for the ratio of the matrix elements appearing in Eq. (12) is obtained. Upon substitution, the result is

$$(2\ell + 1)\langle y_1 | F_\ell(r) | y_2 \rangle \approx \frac{k^{\ell-1}}{\ell(2\ell - 1)!!} \langle y_1 | r^\ell | y_2 \rangle \times \left\{ 1 - \frac{\ell \xi^2}{2(\ell + 2)(2\ell + 3)c^2} \times (A_\ell + B_\ell P_\ell^{\ell-1} + C_\ell R_\ell^{\ell-1} + D_\ell R_\ell^{\ell-2}) \right\}. \quad (13)$$

The symbols P and R are ratios of the integrals and are defined in Eq. (A15). They are smaller than unity.

The quantity ξ is crucial, since it distinguishes between on- and off-resonance couplings. It is defined by

$$\xi \equiv \frac{\omega}{\varepsilon_2 - \varepsilon_1}. \quad (14)$$

A. On-resonance couplings

For $\omega = \varepsilon_2 - \varepsilon_1$ —i.e., when the photon frequency equals the energy difference of the two states— ξ is equal to unity.

The presence of c^2 in the denominator of Eq. (13) renders the second term small. The first component of the second term is the only one that depends on the energies—i.e.,

$$A_\ell = \frac{1}{2}(\varepsilon_2 - \varepsilon_1)[(\ell + 1)(\ell + 2) + b] - 2\varepsilon_2(\ell + 1)(\ell + 2). \quad (15)$$

According to Eq. (A5), $b = \ell_2(\ell_2 + 1) - \ell_1(\ell_1 + 1)$.

Rydberg initial state. For the dipole-allowed transitions $\ell = 1$, the ratios are almost independent of the principal quantum number of the Rydberg state in the test region around $n = 50$ (they decrease very slowly with increasing n), and the same is true for the A_ℓ component since ε_1 , being the energy of the Rydberg state, is close to zero. The most important ratio is R_1^0 which is equal to 0.2, while the other two are an order of magnitude smaller. Thus, for ε_2 equal to 0.5 a.u. and $\xi = 1$, the correction to the EDA is of the order of 10^{-6} . It is stressed that this result is nearly independent of the initial state.

In other words, for a value of k of the order of up to tens of eV, the first term of Eq. (13) dominates regardless of the value of $k\langle y_1 | r | y_1 \rangle$, which can be made arbitrarily larger than unity by starting with a Rydberg state of a sufficiently high n .

Thus, here, the usual LWA argument—namely $kr \ll 1$, where r is “of the order of atomic dimensions”—appears to be a sufficient but not a necessary condition.

B. Off-resonance couplings

On the other hand, for *off-resonance* transitions, ξ can be made quite large. We will consider two examples.

(1) For $\omega = 0.5$ a.u., the off-resonance transition matrix element from a high (e.g., $n = 50$) Rydberg state to the states close to the threshold of the continuous spectrum is substantially different when using the dipole instead of the full operator (about 10%). Specifically, for transitions to the threshold ($\varepsilon_2 = 0$), the value of ξ is 2500 and the correction is approximately 0.07. The ensuing correction in absolute values is quite important since, in this case, the first term is of the order of 10^5 . (It falls quickly as ε_2 increases.)

Interesting special case. A more drastic case is when there are intrashell couplings ($\xi = \infty$), which is the situation that was encountered in the nonperturbative calculations of [2]. In Fig. 3 we plot the multipolar interaction matrix element as a function of the angular momentum of the final state, starting from $50p$. I.e., we show the slow convergence to zero of the $50p \rightarrow 50\ell$ matrix elements as ℓ increases. It is seen that the absolute value of the full interaction operator matrix element is a slowly decreasing function of ℓ and retains a substantial magnitude for values of ℓ way beyond 1. The calculation of these matrix elements involves, as ℓ increases, an increasing number of terms of the expansion (6).

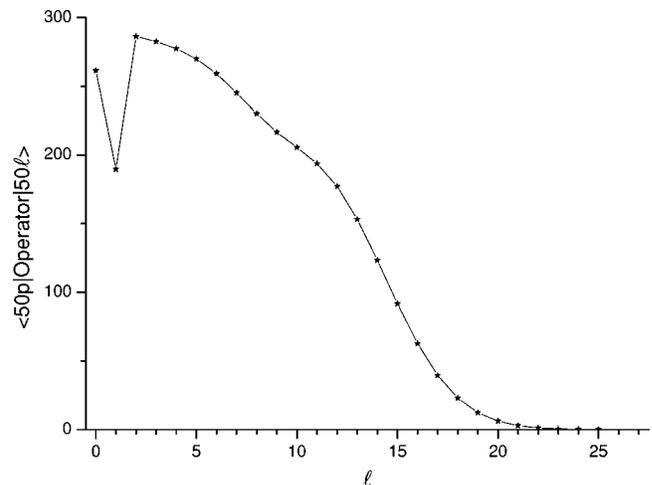


FIG. 3. Absolute value of the multipolar matrix element [time factor and complex conjugation as in Eq. (6) are not included] as a function of the angular momentum ℓ of the final state ($n = 50$, $m = 0$), starting from $50p$ ($m = 1$).

V. SYNOPSIS AND CONCLUSIONS

As laser spectroscopy is enriched with new possible short pulses, phenomena involving high-lying Rydberg states either as initial states in multistep excitation processes or as intermediates during nonlinear coherent processes with large photons become feasible. In such cases, both on- and off-resonance radiative couplings play a role. Since both Rydberg and scattering stationary states are described by extended wavefunctions, the normal consequences of the long-wavelength approximation cannot be taken for granted. For example, previous results from formal analysis and from the solution of the time-dependent Schrödinger equation (TDSE) showed significant differences in specific processes involving off-resonance couplings between the electric dipole approximation and the full-interaction multipolar Hamiltonian [1,2].

Given the significance of the heuristic quantity kr [see condition (3)], here we focused on the r part—namely, on amplitudes where both initial- and final-state wave functions are extended. As a typical example, we chose as initial states the $n = 50$ and $n = 80$ Rydberg wave functions of hydrogen, computed numerically. We point out that preparation of such states as part of a wave packet may affect the physics of a particular overall process but not the conclusions regarding the individual matrix elements studied here.

The herein numerical and analytic results lead to the following conclusions.

(i) For on-resonance transitions from the $n = 50$ and 80 Rydberg states (about 13.574 eV above the ground state), to the continuum, with photoelectron energy up to 1 a.u., the ratio of the dipole/quadrupole matrix elements in the LWA drops from approximately 10^4 at threshold to 1.0×10^2 at 1 a.u. This fast deterioration of the EDA results from the large extent of the Rydberg wave function and is expected to be present in coherent or incoherent multistep ionization processes where the last step involves a high Rydberg state of an atom or an ion and is induced by optical, UV, or more energetic photons.

(ii) Even when the LWA condition $kr \ll 1$ is not satisfied, the higher-order corrections to each level of the multipole series of the LWA—i.e., corrections to the dipole, quadrupole, etc., matrix elements—are very small for each bound-free transition, provided $\xi \equiv \omega/(\varepsilon_2 - \varepsilon_1)$ [Eq. (14)] is close to unity. In other words, for such cases the LWA is a sufficient but not a necessary condition for the validity of the EDA.

(iii) For processes involving off-resonance couplings, the EDA and higher multipole expressions of the LWA fail more readily. The larger ξ is, the greater is the discrepancy between the EDA and the full interaction. The extreme case corresponds to intrashell couplings, where $\varepsilon_2 = \varepsilon_1$ (or $\varepsilon_2 \approx \varepsilon_1$ for nearly hydrogenic spectra). For example, for the case of the $n=50$ hydrogen shell, if we start with $50p$, the matrix element involves not only orbital angular momenta with $\Delta\ell = \pm 1$, but a series of them, $50p \rightarrow 50\ell$, up to $\ell=21$. Among various possibilities, such matrix elements are present in off-resonance couplings which enter in schemes of Rydberg wave packet production such as those discussed in [1,2] or in multiphoton transitions in neutral or ionized atoms where Rydberg and scattering states are involved in higher orders.

Finally, we note that the analysis herein does not pertain to continuum-continuum matrix elements, which play an important role in above threshold ionization (ATI). Actually, for continuum-continuum transitions, the magnitude of the EDA matrix elements differs from the ones obtained with the full electric field operator, not only quantitatively but also qualitatively [1]. On the other hand, the model of classical trajectories and of dipole interaction near the nucleus [14,15] is considered by many researchers sufficient for the treatment of phenomena such as ATI and high-order harmonic generation, suggesting that the relevant physics is taking place near the nucleus, where the LWA and EDA work. Nevertheless, a reliable and thorough understanding can come only after accurate solutions of the quantum mechanical TDSE for real systems, using both the full operator and EDA, are compared with details of accurate experiments.

APPENDIX

We define

$$H_i = \frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r}, \quad i=1,2, \quad (\text{A1})$$

so that

$$H_i y_i = -2\varepsilon_i y_i. \quad (\text{A2})$$

Consider the integral

$$\int_0^\infty y_1 (H_1 r^n - r^n H_2) y_2 dr. \quad (\text{A3})$$

After rearrangement of the first term in (A3) and integration by parts this is equal to

$$[ny_1 r^{n-1} y_2 + r^n (y_1 y_2' - y_1' y_2)]_0^\infty + 2(\varepsilon_2 - \varepsilon_1) \int_0^\infty y_1 r^n y_2 dr. \quad (\text{A4})$$

On the other hand, the commutator $(H_1 r^n - r^n H_2)$ is given by

$$(H_1 r^n - r^n H_2) = [n(n-1) + b] r^{n-2} + 2nr^{n-1} \frac{d}{dr}, \quad (\text{A5})$$

where $b = l_2(l_2+1) - l_1(l_1+1)$.

In the case where one of the y_i is a bound function the quantity inside the square brackets in (A4) is zero while for continuum-continuum transitions it gives rise to δ functions; see [2]. Therefore,

$$(\varepsilon_2 - \varepsilon_1) \langle y_1 | r^n | y_2 \rangle = \frac{1}{2} [n(n-1) + b] \langle y_1 | r^{n-2} | y_2 \rangle + n \langle y_1 | Q^{n-1} | y_2 \rangle, \quad (\text{A6})$$

where $Q^n = r^n d/dr$. Similarly, by considering the integral

$$\int_0^\infty y_1 (H_1 Q^n - Q^n H_2) y_2 dr, \quad (\text{A7})$$

we find that, after rearrangement, it is equal to

$$[ny_1 Q^{n-1} y_2 + (y_1 Q^n y_2' - y_1' Q^n y_2)]_0^\infty + 2(\varepsilon_2 - \varepsilon_1) \int_0^\infty y_1 Q^n y_2 dr, \quad (\text{A8})$$

while the commutator is given by

$$(H_1 Q^n - Q^n H_2) = [n(n-1) + b] Q^{n-2} - 4n\varepsilon_2 r^{n-1} - 2(2n-1)z r^{n-2} + 2(n-1)l_2(l_2+1) r^{n-3}. \quad (\text{A9})$$

In the case where one of the y_i is a bound function, we obtain

$$(\varepsilon_2 - \varepsilon_1) \langle y_1 | Q^n | y_2 \rangle = \frac{1}{2} [n(n-1) + b] \langle y_1 | Q^{n-2} | y_2 \rangle - 2n\varepsilon_2 \langle y_1 | r^{n-1} | y_2 \rangle - (2n-1)z \langle y_1 | r^{n-2} | y_2 \rangle + (n-1)l_2(l_2+1) \langle y_1 | r^{n-3} | y_2 \rangle. \quad (\text{A10})$$

Combining Eqs. (A6) and (A10) we arrive at the relation

$$(\varepsilon_2 - \varepsilon_1)^2 \langle y_1 | r^n | y_2 \rangle = A_{n-2} \langle y_1 | r^{n-2} | y_2 \rangle + B_{n-2} \langle y_1 | Q^{n-3} | y_2 \rangle + C_{n-2} \langle y_1 | r^{n-3} | y_2 \rangle + D_{n-2} \langle y_1 | r^{n-4} | y_2 \rangle, \quad (\text{A11})$$

where

$$A_{n-2} = \frac{1}{2} (\varepsilon_2 - \varepsilon_1) [n(n-1) + b] - 2\varepsilon_2 n(n-1) \quad (\text{A12})$$

and

$$B_{n-2} = \frac{n}{2}[(n-1)(n-2) + b], \quad C_{n-2} = -n(2n-3)z, \\ D_{n-2} = n(n-2)l_2(l_2+1). \quad (\text{A13})$$

The transition matrix element of the n th power of r is expressed, in Eq. (A11), in terms of similar matrix elements of lower powers. It is useful to write this equation in terms of ratios as

$$(\varepsilon_2 - \varepsilon_1)R_{n-2}^n = A_{n-2} + B_{n-2}P_{n-2}^{n-3} + C_{n-2}R_{n-2}^{n-3} + D_{n-2}R_{n-2}^{n-4}, \quad (\text{A14})$$

where

$$R_m^n = \frac{\langle y_1 | r^n | y_2 \rangle}{\langle y_1 | r^m | y_2 \rangle}, \quad P_m^n = \frac{\langle y_1 | Q^n | y_2 \rangle}{\langle y_1 | r^m | y_2 \rangle}. \quad (\text{A15})$$

For $m > n$, the ratios are expected to be smaller than unity and calculations show this to be a fact.

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