On- and off-resonance radiation-atom-coupling matrix elements involving extended atomic wave functions

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In continuation of our earlier works, we present results concerning the computation of matrix elements of the multipolar Hamiltonian (MPH) between extended wave functions that are obtained numerically. The choice of the MPH is discussed in connection with the broader issue of the form of radiation-atom (or -molecule) interaction that is appropriate for the systematic solution of various problems of matter-radiation interaction. We derive analytic formulas, in terms of the sine-integral function and spherical Bessel functions of various orders, for the cumulative radial integrals that were obtained and calculated by Komninos, Mercouris, and Nicolaides [Phys. Rev. A **71**, 023410 (2005)]. This development allows the much faster and more accurate computation of such matrix elements, a fact that enhances the efficiency with which the time-dependent Schrödinger equation is solved nonperturbatively, in the framework of the state-specific expansion approach. The formulas are applicable to the general case where a pair of orbitals with angular parts $|\ell_1, m_1\rangle$ and $|\ell_2, m_2\rangle$ are coupled radiatively. As a test case, we calculate the matrix elements of the electric field and of the paramagnetic operators for on- and off-resonance transitions, between hydrogenic circular states of high angular momentum, whose quantum numbers are chosen so as to satisfy electric dipole and electric quadrupole selection rules. Because of the nature of their wave function (they are nodeless and the large centrifugal barrier keeps their overwhelming part at large distances from the nucleus), the validity of the electric dipole approximation in various applications where the off-resonance couplings must be considered becomes precarious. For example, for the transition from the circular state with $n = 20$ to that with $n = 21$, for which $\langle r\rangle \approx 400$ a.u., the dipole approximation starts to fail already at XUV wavelengths ($\lambda < 125$ nm).

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I. INTRODUCTION

Rydberg states, whose outer orbital resembles hydrogen eigenfunctions with a quantum defect in their energies, dominate the discrete spectrum of atoms (molecules) and their positive ions. Therefore, it is reasonable to expect that, under suitable circumstances of atomic (molecular) energy spectra and the parameters of a radiation pulse that interacts with an atom (molecule) (i.e., wavelength, temporal duration and shape, and intensity), they may play a distinct role in the processes of excitation and ionization by absorption of one or more photons. The formal and computational examination of such a possibility can be carried out within time-independent or time-dependent frameworks, depending on the problem.

In previous publications [1–3], we presented formal and numerical results from the implementation of the full electric interaction of the multipolar Hamiltonian (MPH) [4–7] to the calculation of radiative coupling matrix elements involving atomic Rydberg wave functions. The interaction energy present in the MPH involves the coupling of the atom to the electric and magnetic fields, which are gauge-independent physical quantities. In the electric dipole approximation (EDA), it is reduced directly to $-e\vec{E}(t)\cdot\vec{r}$, where $\vec{E}(t)$ is the field without dependence on coordinates. Hence the corresponding coupling matrix elements involve the length form of the EDA $\langle n|\vec{r}|m\rangle$.

The calculated matrix elements of the full electric interaction and of the EDA were used for the quantitative treatment of the time-dependent excitation by a weak pulse of Rydberg wave functions (wave packets) [2]. This was done by computing nonperturbatively the solution $\Psi(t)$ of the time-dependent Schrödinger equation (TDSE) via the state-specific expansion approach (SSEA). For a review of the SSEA, with a selection of prototypical applications to atomic and diatomic systems, see [8].

In the present paper, we continue the exploration of the use of the MPH for the calculation of Rydberg-Rydberg matrix elements. We have already derived and implemented analytic formulas for the cumulative radial integrals in terms of which matrix elements of the MPH have been calculated [1–3]. As we show in Appendix A, these integrals are expressed as combinations of the sine-integral function and spherical Bessel functions of various orders. This has the advantage of both speed and accuracy in their calculation since excellent algorithms and implementation routines are available for these functions in the literature [9]. The formulas can be applied for the treatment of the general case where a pair of orbitals with angular parts $|\ell_1, m_1\rangle$ and $|\ell_2, m_2\rangle$ are coupled radiatively. The radial part of these orbitals can be either a hydrogenic function (used in analytic or numerical form) or a numerical one obtained using a fixed term-dependent potential. [We have been using Hartree-Fock (HF) or multiconfigurational HF potentials.] We recall that for sufficiently high angular momenta ($\ell \geqslant 5$) the outer atomic orbitals are practically hydrogenic.

We have used as test case hydrogenic circular states of high angular momentum [10,11], with quantum numbers

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appropriate for transitions satisfying electric dipole and electric quadrupole selection rules. The circular states are nodeless. They are those for which, at a given energy level n, $|m|$ and ℓ have their maximum value, i.e., $|m| = \ell = n - 1$. We note that the dipole-allowed transition for circular states of the transition $n = 29 \rightarrow n = 30$ at 256 GHz was used in the experimental study of Lutwak *et al*. [11].

For the calculation of the $3j$ symbols with very large arguments $\ell \geqslant 30$, which appear in the angular factors, a method was implemented that circumvents the problem of the numerical overflows that arise with the commonly used computational routines. Specifically, Tuzun *et al*. [12] have rewritten the definition formula of the $3j$ symbols with $m_1 = m_2 = m_3 = 0$ in a clever way that avoids numerical overflows.[1] For the most general case, we implemented a recursion formula [13].

We stress that, although the test cases are chosen for hydrogen, the wave functions are obtained and used numerically. The use of numerical orbitals presents additional difficulties for the mathematics and computation of radiation-atom-coupling matrix elements with extended Rydberg and scattering wave functions, mainly because of the appearance of highly oscillatory integrands and on-shell singularities [1–3,8,14,15]. However, they are necessary for the economic and transparent treatment of processes in arbitrary many-electron atoms, for which state-specific orbitals in the discrete and the continuous spectra must be computed numerically (assisted, when necessary, by Wentzel-Kramers-Brillouin techniques), in a symmetry-adapted $(N–1)$-electron core potential. Obviously, in the case of hydrogen, no electron core is present.

A. Radiation-atom-coupling matrix elements in connection with the characteristics of the unperturbed spectrum

The MPH is related to the minimal coupling Hamiltonian (MCH) [which involves the vector potential $\vec{A}(\vec{r},t)$ and is the one usually invoked in studies of spectroscopy and quantum optics] via a unitary (canonical) transformation [4–7]. As shown in [7], this relation entails the general result that "... the matrix elements for energy-conserving processes (i.e., on the energy shell) calculated using the multipolar and minimal coupling Hamiltonians are equal." As a tangible example of the utility of the formalism that will be presented in Sec. II, in Appendix B we demonstrate this equality analytically for the case of the $1s \rightarrow 2p_1$ one-photon transition in hydrogen.

The arguments for carrying out the development of formalism and its numerical implementation for the computation of Rydberg-Rydberg matrix elements of the MPH and the corresponding EDA length operator were presented in [1–3]. One of the main objectives was to explore aspects of the degree of validity of the EDA since, as we stated, "... results on field-induced processes that involve such extended states and are based on the electric dipole approximation cannot be justified *a priori*" [1]. The same concern had been expressed earlier in [14] in connection with free-free transition matrix elements, a topic that we also investigated recently from a different perspective [15]. In connection with the solution of the TDSE for excitation of hydrogen Rydberg states, where off-resonance coupling matrix elements play a significant role [1,2], our conclusion was phrased as follows: "Already for $n = 25$ the differences [between the EDA and the full electric operator] are very significant, and force us to suggest that it is doubtful whether the theory and understanding of Rydberg wavepacket [*sic*] formation and dynamics is reliable within the framework of the EDA" [1].

At this point, having mentioned the MPH and the length form of the EDA, it is worth recalling that there are alternative expressions that are formally equivalent in the framework of theoretical spectroscopy. At the level of the full-interaction Hamiltonian, the alternative to the MPH is the MCH, while at the level of the EDA there are (at least) two more operators, the velocity and the acceleration, that are considered in various nonrelativistic formulations and calculations. The word "equivalent" here means that for a given measurable quantity the use of the alternative forms will produce the same results provided the necessary theoretical requirements are fulfilled, such as the use of complete sets of exact wave functions or the phase change of $\Psi(t)$ by an appropriate gauge transformation, if this is necessary.

However, in actual EDA calculations on N-electron systems, the wave functions are not exact and when needed in time-independent perturbative expressions or in the direct solution of the TDSE, the sets of function spaces are not complete. Actually, the issue of the lack of completeness becomes more acute as the intensity of the radiation increases. Therefore, the results from the use of the three EDA operators are in general different.

Although the above requirements of exactness of wave functions and completeness of corresponding expansions are normal constraints of quantum mechanics, the discrepancies among the computed results using the different operators have provided reasons, over several decades, for a plethora of discussions and analyses, including the theme of determining and/or of favoring one of the expressions for radiation-atom coupling as the formally more appropriate interaction operator. The recent review article [8] contains a number of publications in which various aspects of this issue are discussed, often as a result of disagreement as to its proper understanding and resolution of possible dilemmas.

Our position on this matter, which led to the choice of the MPH and the corresponding EDA length form in our approach to the problem of Rydberg state excitation [1,2], is as follows.

(i) At the fundamental level of theory, the choice of the MPH and the corresponding EDA length form $-e\vec{E}(t)\cdot\vec{r}$ ensures that the TDSE is gauge independent since the interaction terms in the Hamiltonian contain only the fields and not the vector potential. Therefore, the state-specific time-dependent expansion coefficients in the SSEA are computed directly as occupation probability amplitudes for the state to which they correspond and there is no need to worry about a gauge transformation of the first kind on $\Psi(t)$ [16,17]. [On the other hand, even if the interaction were hypothetically taken to involve the full $\vec{A}(\vec{r},t)$ or more realistically the EDA form of the MCH, i.e., $\frac{e}{mc}\vec{p}\cdot\vec{A}(t)$, it is possible in practice to avoid

[1]We point out that in their Eq. (13), the first term in the numerator of the second product should contain C instead of A.

the phase transformation of $\Psi(t)$ by choosing the solutions of the TDSE at the points of time over a field cycle where $\vec{A}(t)$ vanishes, including the beginning and the end of the pulse.]

(ii) The root cause of the disagreement in results obtained with different EDA operators for the same problem, either in time-independent or in time-dependent frameworks, is the inevitable recourse to the use of approximate and incomplete function spaces, except, occasionally, in simple cases involving the hydrogen atom. In order for actual calculations to have a good convergence and a reasonable degree of accuracy with respect to the (computationally elusive) exact answer, the choice of the interaction operator must take into account the interconnection of the characteristics of the operator and the space of wave functions on which it acts.

Of course, for complex systems and complex problems that engage many states, the above may not be easy to secure consistently, at least *a priori*. Some trial and error may be needed. In contrast, for the case of one-photon transition probabilities, where only two wave functions are involved and the matrix element is on resonance, things are simplified and the matrix element may be scrutinized to a good approximation. This case was discussed four decades ago and the arguments and conclusions were based on many-electron calculations of one-photon electric dipole transition rates (oscillator strengths) in systems where, in fact, electron correlation, i.e., beyond the nonlocal Hartree-Fock approximation, is important. The results were tested for the length, velocity, and acceleration operators [18].

In the case of processes of higher order, such an analysis becomes more complicated. Now one must pay attention to the interplay between characteristics of the interaction operator and a small or a large set of wave functions in the spectrum of the unperturbed Hamiltonian $\boldsymbol{H}_0$. For example, as already mentioned, the results of [1–3] showed that, when Rydberg-Rydberg or Rydberg-scattering couplings are involved, terms from the full electric operator, which are additional to the EDA operator and subject to the same selection rules, contribute significantly in off-resonance couplings (with respect to the radiation wavelength). This conclusion was reached in steps, based on the consideration of the nature of the problem. In the first step we concluded that the physics of the time-dependent excitation of the Rydberg states is best revealed using the $-e\vec{E}(t)\cdot\vec{\boldsymbol{r}}$ interaction of the EDA, which corresponds to the MPH, rather than using the $-\frac{e}{mc}\vec{\boldsymbol{p}}\cdot\vec{A}(t)$ interaction (velocity form), which corresponds to the MCH.

Specifically, the problem had to do with the quantitative determination of the time-dependent excitation of hydrogen Rydberg states [1,2]. For this type of excitation process, off-resonance coupling matrix elements among high-lying orbitals play a significant role. In this context, by first analyzing the problem in terms of the EDA, it is seen that convergence of the calculation is considerably better if the EDA has the length form $\langle n|\vec{\boldsymbol{r}}|m\rangle$. This conclusion is reachable before any computation by considering the fact that the most important mixing to the directly excited state (on resonance with the center of the pulse) has to come from neighboring states. Of these off-resonance matrix elements, the most important ones in hydrogen are the intrashell ones (same n, coupled subject to $\Delta\ell=\pm1$), which are given by $-\frac{3}{2}n\sqrt{n^2-\ell^2}$ (regardless of the coordinate system, spherical or parabolic). On the contrary, in the EDA velocity form $\langle n|\vec{\boldsymbol{p}}|m\rangle$, they are zero. Therefore, in the latter case the convergence towards the accurate solution must be effected by including in the expansion a huge number of higher-lying states of the Rydberg and the continuous spectra.

II. REDUCTION OF THE MULTIPOLAR HAMILTONIAN TO WORKABLE EXPRESSIONS FOR ATOMIC MATRIX ELEMENTS

A. Electric-field operator

The electric part of the MPH can be written elegantly as [6,7]

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

where $\vec{\kappa}$ is the wave vector. With $\vec{\varepsilon}$ as the polarization vector, the electric field is written as

$$\vec{E}=\tfrac{1}{2}E_0(t)\,\vec{\varepsilon}e^{i\vec{\kappa}\vec{r}-i\omega t}+\text{c.c.} \tag{2}$$

The simplest case arises when the z axis is chosen in the direction of the wave vector $\vec{\kappa}$. Then, by convention, the polarization $\vec{\varepsilon}$ of the electric field is along the x axis.

Using (2), the general formula (1) can be reduced, in the case of atoms, to an expression in terms of integrals of spherical Bessel functions multiplied by an angular part containing spherical harmonics [1]. In that paper we showed that the electric-field operator can be written in the form

$$\begin{aligned}H_{\rm el}&=\frac{1}{2}E_0(t)e^{-i\omega t}\sum_{\ell=1}^{\infty}i^{\ell+1}(2\ell+1)F_\ell(\kappa r)\Theta_\ell(\theta,\phi)+\text{c.c.}\\&\equiv\frac{1}{2}E_0(t)e^{-i\omega t}O_E(\kappa,\vec{r})+\text{c.c.},\end{aligned} \tag{3}$$

where $E_0(t)$ is the amplitude of the electric field with wave vector κ,

$$F_\ell(\kappa r)=\frac{1}{\kappa}\int_0^r\frac{1}{r'}j_\ell(\kappa r')dr', \tag{4}$$

with $j_\ell(\kappa r')$ the spherical Bessel function, and

$$\Theta_\ell(\theta,\phi)=\sqrt{\frac{\pi\ell(\ell+1)}{2\ell+1}}\left(Y_\ell^{-1}-Y_\ell^{1}\right), \tag{5}$$

with Y_ℓ^1 the spherical harmonic. The angular part causes transitions with $\Delta m=\pm1$.

We are interested in the computation of matrix elements between atomic states of definite angular momentum. Hence we perform the angular integration first. The resulting radial operator is given by

$$\begin{aligned}O_{\ell_1m_1;\ell_2m_2}(r)&=\left\langle Y_{\ell_1}^{m_1}\middle|O_E(\kappa,\vec{r})\middle|Y_{\ell_2}^{m_2}\right\rangle\\&=\sum_{\ell=1}^{\infty}i^{\ell+1}(2\ell+1)F_\ell(\kappa r)\left\langle Y_{\ell_1}^{m_1}\middle|\Theta_\ell(\theta,\phi)\middle|Y_{\ell_2}^{m_2}\right\rangle.\end{aligned} \tag{6}$$

Here Θ_ℓ, as given by Eq. (5), contains $Y_\ell^{\pm1}$. Therefore, the result of the angular integration over the spherical harmonics

of the initial and the final state can be expressed in terms of $3j$ symbols. To this purpose, we use the formula [19]

$$\left\langle Y_{\ell_1}^{m_1}\middle|Y_{\ell}^{\pm 1}\middle|Y_{\ell_2}^{m_2}\right\rangle = \left[\frac{1}{4\pi}(2\ell_1+1)(2\ell_2+1)(2\ell+1)\right]^{1/2} \times \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ -m_1 & m_2 & \pm 1 \end{pmatrix}. \tag{7}$$

Hence the angular matrix element in Eq. (6) is given by

$$\left\langle Y_{\ell 1}^{m_1}\middle|\Theta_\ell(\theta,\phi)\middle|Y_{\ell 2}^{m_2}\right\rangle = \frac{1}{2}[(2\ell_1+1)(2\ell_2+1)\ell(\ell+1)]^{1/2} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} \times \left[\begin{pmatrix} \ell_1 & \ell_2 & \ell \\ -m_1 & m_2 & -1 \end{pmatrix} - \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ -m_1 & m_2 & 1 \end{pmatrix}\right]. \tag{8}$$

According to the selection rules for the $3j$ symbols, $m_2 = m_1 \pm 1$. Therefore, only one of the symbols in the set of large square brackets in Eq. (8) is nonzero. Furthermore, $|\ell_1 - \ell_2| \leqslant \ell \leqslant \ell_1 + \ell_2$, while the first symbol in Eq. (7) requires that $\ell_1 + \ell_2 + \ell$ is even. In every other case the $3j$ symbols are zero. Consequently, the infinite summation over ℓ is reduced to a finite one. For transitions with $|\ell_1 - \ell_2| = 1$ (electric dipole selection rule), ℓ acquires odd values. For transitions with $|\ell_1 - \ell_2| = 2$ (electric quadrupole selection rule), ℓ acquires even values.

Equation (8) is the analytic expression of the coefficients of the $F_\ell(\kappa r)$ integrals, which are the components of the radial operator (6). The spherical Bessel functions of the integrand can be expressed as infinite polynomials. For small values of the argument κr, we may keep, to a good approximation, the first few powers only. This is the long-wavelength approximation (LWA) whose use in quantum mechanics is extensive and pervades many fields, especially in the form of the EDA and the electric quadrupole approximation (EQA), where only the smallest power of κr in the expansion is kept.

Setting $j_\ell(x) \approx \frac{x^\ell}{(2\ell+1)!!}$, one obtains $(2\ell+1)F_\ell(\kappa r) \approx \kappa^{\ell-1}\frac{r^\ell}{\ell(2\ell-1)!!}$. For the EDA, the first term $\ell = 1$ of the expansion with odd values of ℓ gives $3F_1 \approx r$. For the EQA, the first term $\ell = 2$ of the expansion with even values of ℓ gives $5F_2 \approx \frac{1}{6}\kappa r^2$.

Higher-order multipoles get contributions from more than one term. For example, the octupole results from the second term in the expansion of $j_1(x)$ and the first term of $j_3(x)$.

As has been widely written since the beginning of the quantum mechanical theory of atom-radiation interaction, the EDA and the EQA (different selection rules) are considered valid based on the heuristic inequality $\kappa r \ll 1$, where r represents the dimensions of the atom. In fact, since we are dealing with transition matrix elements between two states, this argument is more properly expressed by stating that at least one of the wave functions entering the matrix element is compact, i.e., the ground or low-lying excited states.

In contrast, it is also possible to have problems, especially those corresponding to high-order processes with off-resonance matrix elements, where the two states of the transition matrix element have bound yet very extended wave functions. This is always the case with Rydberg states. The question then arises as to what degree the operators of the EDA and the EQA are valid in such cases. To answer this question we compare, in Sec. III, the matrix elements of both the MPH and the EDA and EQA operators between two highly excited circular states as a function of κ.

B. Paramagnetic-field operator

The paramagnetic part of the MPH is written as [6,7]

$$H_{\rm par} = \frac{e}{2c}\sum_j \int_0^1 [\vec{r}_j \times \vec{p}\vec{B}(\lambda\vec{\kappa}\cdot\vec{r}_j) + \vec{B}(\lambda\vec{\kappa}\cdot\vec{r}_j)\vec{r}_j \times \vec{p}]\lambda\, d\lambda \equiv \frac{e}{2c}\sum_j \int_0^1 [\vec{l}\vec{B}(\lambda\vec{\kappa}\cdot\vec{r}_j) + \vec{B}(\lambda\vec{\kappa}\cdot\vec{r}_j)\vec{l}]\lambda\, d\lambda. \tag{9}$$

As in the case of the electric field, the z axis is chosen in the direction of the wave vector $\vec{\kappa}$, while the polarization of the magnetic field is along the y axis.

As it was shown in [1], using for the magnetic field an expansion similar to the one for the electric field (2), the paramagnetic field operator has a form resembling that of Eq. (3):

$$H_{\rm par} = \frac{1}{2c}B_0(t)e^{-i\omega t}\sum_{\ell=0}^{\infty} i^\ell(2\ell+1)F_\ell(\kappa r)\Theta_\ell(\theta,\phi) + \text{c.c.} \equiv \frac{1}{2c}B_0(t)e^{-i\omega t}O_B(\kappa,\vec{r}) + \text{c.c.}, \tag{10}$$

where $B_0(t)$ is the amplitude of the magnetic field with wave number κ and

$$F_\ell(\kappa r) = \frac{1}{(\kappa r)^2}\int_0^{\kappa r} x j_\ell(x)dx, \tag{11}$$

where $j_\ell(x)$ is the spherical Bessel function. The analytic expression for the integrals of Eq. (10) is given in Appendix A. Equation (9) is the analog of Eq. (3). However, the series (9) starts at $\ell = 0$. The function $\Theta_\ell(\theta,\phi)$ has the form[2]

$$\Theta_\ell(\theta,\phi) = \frac{1}{2i}\sqrt{\frac{\pi}{2\ell+1}}\left[-\sqrt{\ell(\ell+1)}\left(Y_\ell^{-1} - Y_\ell^1\right) + 2Y_\ell^0(\hat{l}_+ - \hat{l}_-)\right], \tag{12a}$$

where

$$\hat{l}_\pm Y_\ell^m = \sqrt{(\ell \mp m)(\ell \pm m + 1)}\,Y_\ell^{m\pm 1}. \tag{12b}$$

As in the case of the electric field, the angular part allows transitions with $\Delta m = \pm 1$. The resulting radial operator is nearly identical in form to that of the electric field, i.e.,

$$O_{\ell_1 m_1;\ell_2 m_2}(r) = \left\langle Y_{\ell_1}^{m_1}\middle|O_B(\kappa,\vec{r})\middle|Y_{\ell_2}^{m_2}\right\rangle = \sum_{\ell=0}^{\infty} i^\ell(2\ell+1)F_\ell(\kappa r)\left\langle Y_{\ell_1}^{m_1}\middle|\Theta_\ell(\theta,\phi)\middle|Y_{\ell_2}^{m_2}\right\rangle. \tag{13}$$

However, the function $\Theta_\ell(\theta,\phi)$ is now given by Eq. (12a).

The first term of the angular function in Eq. (12a), call it $\Theta_\ell^{(1)}$, is similar to that of the electric operator (5). The second term, call it $\Theta_\ell^{(2)}$, which contains the raising and lowering

[2]The present Eq. (12a) corrects Eq. (14) of Ref. [1] by a factor of 2.

operators, gives rise to slightly different $3j$ symbols, i.e.,

$$\left\langle Y_{\ell_1}^{m_1}\middle|\Theta_\ell^{(2)}(\theta,\phi)\middle|Y_{\ell_2}^{m_2}\right\rangle = \frac{1}{i}\left[(2\ell_1+1)(2\ell_2+1)\right]^{1/2}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ 0 & 0 & 0\end{pmatrix}\left[\sqrt{(\ell_2-m_2)(\ell_2+m_2+1)}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ -m_1 & m_2+1 & 0\end{pmatrix}\right.$$
$$\left.-\sqrt{(\ell_2+m_2)(\ell_2-m_2+1)}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ -m_1 & m_2-1 & 0\end{pmatrix}\right]. \tag{14}$$

The two terms $\Theta_\ell^{(1)}$ and $\Theta_\ell^{(2)}$ are put on the same footing by expressing the $3j$ symbols of Eq. (8) in terms of the recursion formula

$$-\sqrt{\ell(\ell+1)}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ -m_1 & m_2 & \pm1\end{pmatrix}$$
$$=\sqrt{(\ell_1\pm m_1)(\ell_1\mp m_1+1)}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ -m_1\pm1 & m_2 & 0\end{pmatrix}+\sqrt{(\ell_2\mp m_2)(\ell_2\pm m_2+1)}\begin{pmatrix}\ell_1 & \ell_2 & \ell\\ -m_1 & m_2\pm1 & 0\end{pmatrix}. \tag{15}$$

Only one of the $3j$ symbols in Eq. (14) is nonzero, while both of them are generally nonzero in Eq. (15), due to the selection rules stated above.

Considering the small-r expression of Eq. (11), the same treatment that we applied in the case of the electric field gives

$$(2\ell+1)F_\ell(\kappa r)\approx\frac{(\kappa r)^\ell}{(\ell+2)(2\ell-1)!!}. \tag{16}$$

Comparing this result with Eq. (8) obtained in the case of the electric field, κ appears in the same power as r. Consequently, the term for $\ell=1$, called the magnetic quadrupole, is much smaller than the corresponding one of the electric field for the part of the energy spectrum below the hard x rays ($\kappa=\omega/c$ with $c\approx137$ a.u.) since an additional c^{-1} term is present in Eq. (9).

III. TRANSITIONS BETWEEN CIRCULAR STATES CAUSED BY THE MULTIPOLAR HAMILTONIAN

We shall proceed to calculate off-resonance matrix elements of the MPH between two circular states ($\ell=m=n-1$) connected by electric dipole selection rules. The radial wave function of such a state consists of a single Slater-type orbital with a maximum at $r_{\max}=n^2/Z$. A high value of n produces a large centrifugal barrier that renders the wave function negligible for small distances from the nucleus. As an indicator of the region that contributes the most to the transition probability, we choose the cumulative acceleration integral. This is the matrix element of the r^{-2} operator $\langle n\ell|1/r^2|n'\ell'\rangle$. For hydrogenic atoms, it is equal to $\langle n\ell|r|n'\ell'\rangle(E_n-E'_{n'})^2$. The former operator, being a bound one, is directly amenable to accurate calculation, whereas the latter one is unbound and is extremely inconvenient to handle numerically, especially in the case of scattering states.

For the matrix elements mentioned above, the failure of the LWA starts at XUV wavelengths for the extended wave functions of high n. This result must be compared with the one involving relatively compact wave functions of low n, where the failure appears at much shorter wavelengths, in the region of x ray and beyond.

The matrix element of the EDA operator for the transition $n\to n+1$ between adjacent circular states is given by the analytic expression [20] $R=n^2\frac{(1+1/n)^{n+2}}{Z(1+1/2n)^{2n+5/2}}$.

The limit $R\to n^2e^{1/2n}/Z$ is reached for moderately large n. Note the similarity of this expression with that of the position of the maximum of the lower state. In contrast, the energy difference between adjacent circular states is, to a good approximation, $(1/n^3)(1-3/2n)$. This has an important consequence.

The independent variable of the multipolar operators is κr, where κ is the photon wave number $\kappa=\omega/c$ and c the speed of light, equal to 137.037 a.u. While r is of the order of n^2, κ is of the order of n^{-3} and therefore $\kappa r\sim1/n$. Consequently, since the LWA is valid for $\kappa r\ll1$, we have to consider off-resonance transitions in order to study possibly realistic departures from the predictions of the LWA.

As a case study, we chose to apply the theory to transitions between circular states with $n=20$, 21, and 22. The transition $n=20\to n=21$ is for the electric dipole selection rules and the transition $n=20\to n=22$ is for the electric quadrupole ones.

Figure 1 shows the cumulative acceleration integral, which starts piling up for $r>300$ and reaches a constant at $r=600$. At this radius, the wave functions drop below 10^{-7}. The constant is very close to the exact value of the acceleration integral. Therefore, we consider values of $r\leqslant600$. We also

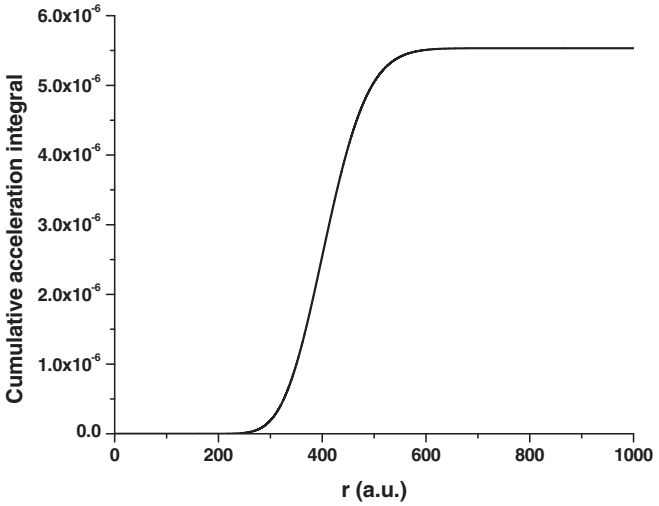

FIG. 1. Integral $\int_0^r u_{n_1\ell_1}(r')(1/r'^2)u_{n_2\ell_2}(r')dr'$ for the hydrogen circular states with $n_1=20$ and $n_2=21$.

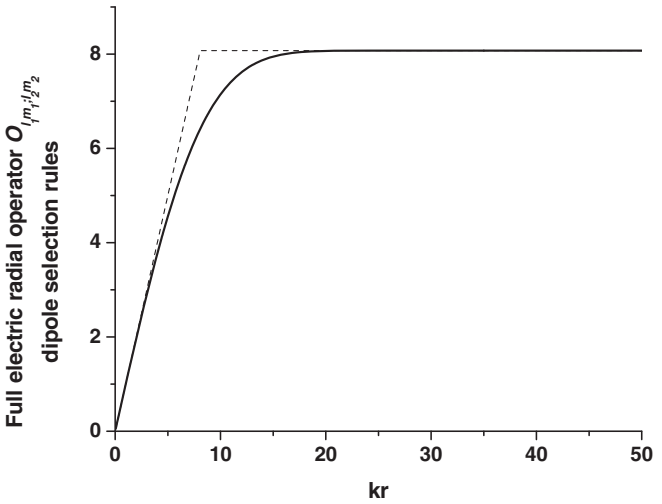

FIG. 2. Full electric radial operator $O_{\ell_1 m_1;\ell_2 m_2}(r) = \langle Y^{m_1}_{\ell_1}|O_E(\kappa,\vec{r})|Y^{m_2}_{\ell_2}\rangle$ [Eq. (6)] for $\ell_1 = m_1 = 19$ and $\ell_2 = m_2 = 20$. The dashed line corresponds to the simplified model proposed in [1].

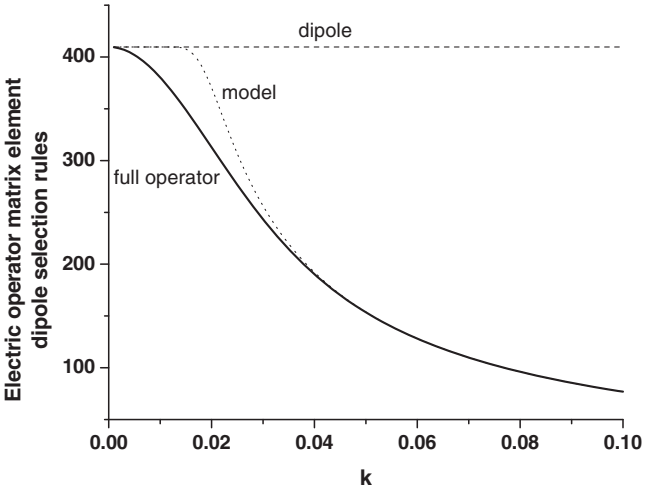

FIG. 4. Full electric operator matrix element for the circular states with $n_1 = 20$ and $n_2 = 21$ as a function of the photon wave number κ in a.u.. The dotted line corresponds to the simplified model of [1]. The horizontal dashed line corresponds to the EDA value. The failure of the EDA for off-resonance matrix elements is striking.

note that for $r \leqslant 250$ the wave functions are negligible due to the centrifugal barrier and the cumulative integral is of the order of 10^{-10}. Hence the region of interest is $250 \leqslant r \leqslant 600$.

In order that $\kappa r > 1$ for $r > 300$, we must have $\kappa > 3.3 \times 10^{-3}$. Then one has corrections to the simple LWA result due to the cubic and higher-order terms resulting from the region $1/\kappa < r < 600$, which, for larger κ values, become the dominant contribution. It is noted that for $\kappa \geqslant 4.0 \times 10^{-3}$, the region where $\kappa r < 1$ requires values of $r < 250$. Therefore, it practically drops out of the calculation. For these wave numbers, the LWA is invalid for the transition under consideration.

Figure 2 shows the full electric radial operator for $n = 20 \rightarrow n = 21$ and Fig. 3 shows the paramagnetic radial operator, as functions of κr. Comparing the two operators, we observe that for large κr the electric one reaches a constant value while the paramagnetic one goes to zero, as it is expected from Eq. (11). The former can be approximated by the simplified model proposed in previous work [1].

Figure 4 shows the matrix element of the full electric radial operator as a function of κ, compared with the constant value of the EDA and the matrix element derived within the simplified model. The failure of the EDA for off-resonance matrix elements is striking. Figure 5 shows the matrix element of the paramagnetic radial operator (magnetic quadrupole selection rules) for various values of κ.

Finally, Fig. 6 shows the full electric radial operator for the transition $20 \rightarrow 22$, which obeys quadrupole selection rules, for various values of κ and a comparison is made with the

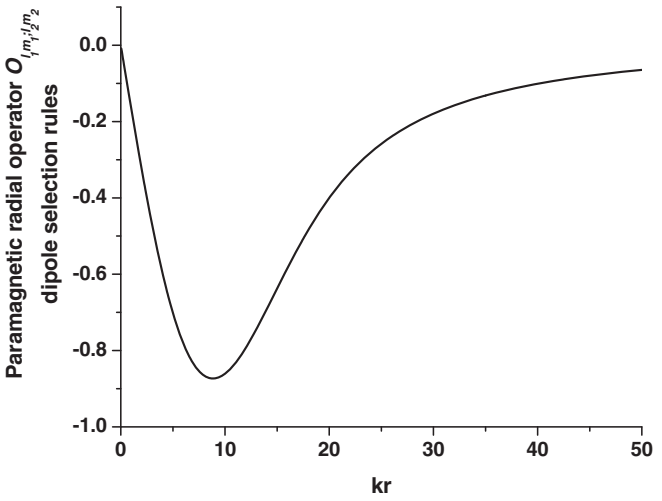

FIG. 3. Paramagnetic radial operator $O_{\ell_1 m_1;\ell_2 m_2}(r) = \langle Y^{m_1}_{\ell_1}|O_B(\kappa,\vec{r})|Y^{m_2}_{\ell_2}\rangle$ [Eq. (13)] for $\ell_1 = m_1 = 19$ and $\ell_2 = m_2 = 20$.

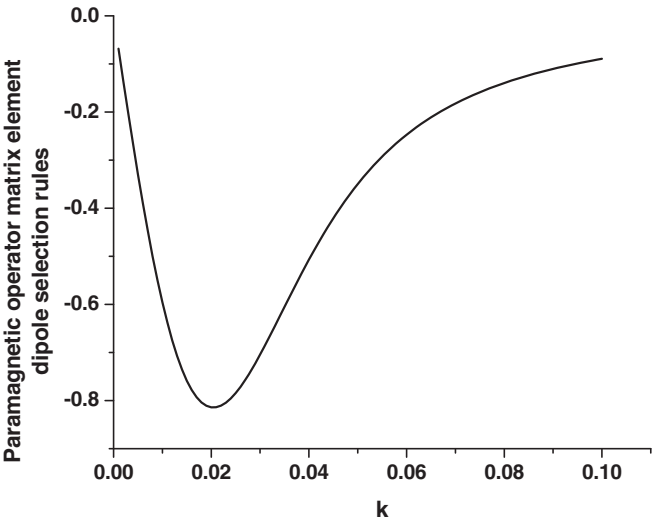

FIG. 5. Paramagnetic operator matrix element for the circular states with $n_1 = 20$ and $n_2 = 21$ as a function of the photon wave number κ in a.u..

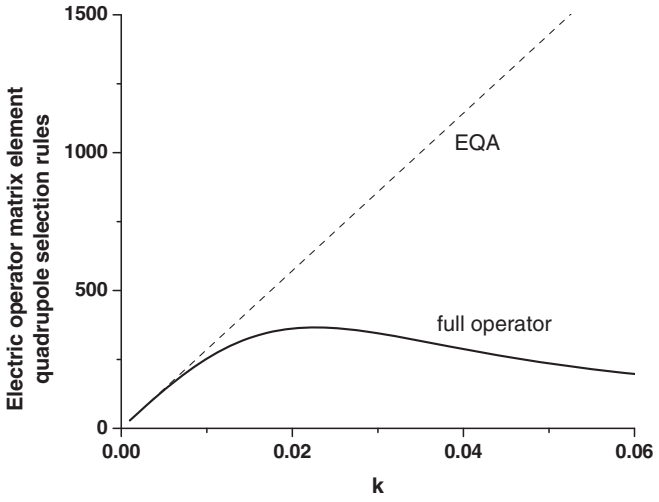

FIG. 6. Full electric operator matrix element for the circular states with $n_1 = 20$ and $n_2 = 22$ as a function of the photon wave number κ in a.u.. The dashed line corresponds to the EQA value. As in the case of the EDA, the deviation from the results of the full operator is striking.

EQA. Here the EQA matrix element increases with increasing energy, while it decreases in the case of the full electric operator. These results show clearly that the EDA and EQA overestimate considerably the value of the transition matrix element for high energies.

IV. CONCLUSION

We have continued our investigation [1–3,8] of properties and numerical methods of computation of matrix elements of the multipolar Hamiltonian [4–7] (electric and paramagnetic operators), subject to selection rules, between extended atomic wave functions that are obtained in numerical form. Such wave functions (i.e., Rydberg bound orbitals and scattering energy-normalized orbitals) must enter into rigorous treatments of a variety of properties and phenomena involving high-order transition processes, i.e., processes whose quantum mechanical description must account for off-resonance coupling matrix elements, induced by the interaction of electromagnetic pulses with atoms.

As explained in the preceding, Eqs. (1), (3), (6), and (8) are the relevant ones for the computation of matrix elements of the electric-field operator and Eqs. (9), (10), (13), and (14) for the paramagnetic one, for a pair of orbitals with angular parts $|\ell_1,m_1\rangle$ and $|\ell_2,m_2\rangle$. Analytic formulas are derived for the radial integrals of Eqs. (3) and (10) in terms of the sine-integral function and the spherical Bessel functions of various orders (Appendix A). For the calculation of these special functions fast and accurate algorithms and implementation routines are available [9]. In addition, the angular part of the electric field and paramagnetic operators [Eqs. (8) and (14), respectively] contains $3j$ symbols that must be calculated efficiently. For $3j$ symbols with very large arguments ($\ell \geqslant 30$), a method was implemented that circumvents the problem of the numerical overflows that arise with the commonly used computational routines. Numerical techniques such as the ones presented here are necessary in order to secure the efficient and accurate computation of the above matrix elements, whose number may run, for certain problems requiring the implementation of the state-specific expansion approach [8] for the nonperturbative solution of the TDSE, in the hundreds of thousands.

The results presented in Figs. 1–6 refer to matrix elements for on- and off-resonance transitions between hydrogenic circular states of high angular momentum, satisfying electric dipole and electric quadrupole selection rules. We note that the paramagnetic quadrupole [$\ell = 1$of Eq. (10)] obeys electric dipole selection rules. For off-resonance couplings the validity of the EDA and EQA is diminishing rapidly (Figs. 4 and 6).

APPENDIX A: INTEGRALS

In the expression of the electric part of the multipolar Hamiltonian, there are integrals of the form

$$I_\ell^{-1}(z) \equiv \int_0^z \frac{1}{x} j_\ell(x) dx \tag{A1}$$

for $\ell > 0$. In order to derive an analytic expression for them, we use the recurrence relations of the spherical Bessel functions [21],

$$\frac{\ell+1}{x} j_\ell(x) = j_{\ell-1}(x) - \frac{\partial}{\partial x} j_\ell(x), \tag{A2a}$$

$$j_{\ell-1}(x) = \frac{\ell-2}{x} j_{\ell-2}(x) - \frac{\partial}{\partial x} j_{\ell-2}(x), \tag{A2b}$$

and

$$j_\ell(x) + j_{\ell-2}(x) = \frac{2\ell-1}{x} j_{\ell-1}(x). \tag{A3}$$

Combining these, we obtain

$$\frac{1}{x} j_\ell(x) = \left(\frac{\ell-2}{\ell+1}\right) \frac{1}{x} j_{\ell-2}(x) - \left(\frac{2\ell-1}{\ell+1}\right) \frac{\partial}{\partial x} \left(\frac{j_{\ell-1}}{x}\right), \tag{A4}$$

which gives, upon integration, the recursive relation

$$I_\ell^{-1}(z) = \frac{\ell-2}{\ell+1} I_{\ell-2}^{-1}(z) - \frac{2\ell-1}{\ell+1} \frac{j_{\ell-1}(z)}{z} + \frac{1}{3}\delta_{\ell 2}, \quad \ell \geqslant 2. \tag{A5}$$

The last quantity is the Kronecker delta and results from $\lim_{z\to 0} \frac{j_1(z)}{z} = \frac{1}{3}$. Equation (A5) is the desired relation, which we utilize in order to derive an analytic expression for the integral (A1). The integrals corresponding to the even values of ℓ start with

$$I_2^{-1}(z) = \frac{1}{3} - \frac{j_1(z)}{z}, \tag{A6}$$

an expression obtained from Eq. (A5) for $\ell = 2$. Note that $\lim_{z\to 0} I_2^{-1}(z) \sim z^3$.

For the integrals corresponding to odd values of ℓ, the value of $I_1^{-1}(z)$ is required. This is obtained from the relation (A2a) for $\ell = 1$ as

$$I_1^{-1}(z) = \tfrac{1}{2}[\mathrm{Si}(z) - j_1(z)], \tag{A7}$$

where $\mathrm{Si}(z) = \int_0^z j_0(x)dx$ is the sine-integral function. Interestingly, the asymptotic behavior of $I_1^{-1}(z)$ has the same form

as Eq. (A6), i.e.,

$$\lim_{z\to\infty} I_1^{-1}(z) = \frac{\pi}{4} - \frac{j_0(z)}{z} + O\left(\frac{1}{z^3}\right), \tag{A8a}$$

while

$$\lim_{z\to 0} I_1^{-1}(z) = \tfrac{1}{3}z + O(z^3). \tag{A8b}$$

Equation (A5) for $\ell > 2$, together with the starting expressions (A7) for the odd ℓ values and (A6) for the even ones, produces the integral $I_\ell^{-1}(z)$ for any value of ℓ and is easily programmable. However, for reasons of clarity we shall also give the explicit expression of $I_\ell^{-1}(z)$. This is written compactly in terms of the double factorials, defined by $(2n)!! = 2\times 4\times\cdots\times(2n) \equiv 2^n n!$ with $(0)!! \equiv 1$ and $(2n+1)!! = 1\times 3\times\cdots\times(2n+1)$ with $(-1)!! \equiv 1$. Let us set $I_0^{-1}(z) \equiv 1$. Then, for $\ell > 1$

$$I_\ell^{-1}(z) = \frac{(\ell-2)!!}{(\ell+1)!!}(p+1)I_p^{-1}(z) - \frac{(\ell-2)!!}{(\ell+1)!!} \times \sum_{\substack{q=1\\ \text{odd}}}^{\ell-1-p} \frac{(\ell-q)!!}{(\ell-q-1)!!}[2(\ell-q)+1)]\frac{j_{\ell-q}(z)}{z}, \tag{A9}$$

where q takes odd values $q = 1,3,\ldots,\ell-1-p$. We define

$$p = \begin{cases} 1 & \text{if} \quad \ell \text{ is odd} \\ 0 & \text{if} \quad \ell \text{ is even} \end{cases} \tag{A10}$$

We note that the even ℓintegrals contain odd-order spherical Bessel functions while the odd ℓintegrals contain even-order ones.

Equation (A8) makes transparent the behavior of the integrals for large values of z. In contrast, in order to examine the behavior of these integrals for small z, it is much simpler to substitute $j_\ell(x) \approx \frac{x^\ell}{(2\ell+1)!!}$ in the original integral equation (A1) and obtain $I_\ell^{-1}(z) \approx \frac{z^\ell}{\ell(2\ell+1)!!}$. It is quite difficult to obtain this result from Eq. (A9) due to the many cancellations involved.

Next, we will examine integrals that appear in the expression of the paramagnetic part of the multipolar Hamiltonian and have the form

$$I_\ell^1(z) \equiv \int_0^z x j_\ell(x)dx. \tag{A11}$$

We wish to derive an analytic expression for these for $\ell > 0$. For $\ell = 0$, one easily obtains $I_0^1(z) = 1 - \cos z$. We employ Eq. (A2b) in the form

$$x j_\ell(x) = \ell j_{\ell-1}(x) - \frac{\partial}{\partial x}(x j_{\ell-1}). \tag{A12}$$

Integrating Eq. (A12), we transform the above integral to a simpler one, defined as

$$I_\ell^0(z) \equiv \int_0^z j_\ell(x)dx. \tag{A13}$$

The relation between the two is

$$I_\ell^1(z) = \ell\, I_{\ell-1}^0(z) - z\, j_{\ell-1}(z). \tag{A14}$$

In order to calculate the $I_\ell^0(z)$ integrals, we use another recurrence relation of the spherical Bessel functions, i.e.,

$$\ell\, j_\ell(x) = (\ell-1)j_{\ell-2}(x) - (2\ell-1)\frac{\partial}{\partial x} j_{\ell-1}(x). \tag{A15}$$

Upon integration we obtain

$$I_\ell^0(z) = \frac{\ell-1}{\ell} I_{\ell-2}^0(z) - \frac{2\ell-1}{\ell} j_{\ell-1}(z) + \delta_{\ell 1}. \tag{A16}$$

The even ℓ series, for $\ell \geqslant 2$, starts with

$$I_0^0 \equiv \int_0^z j_0(x)dx = \mathrm{Si}(z), \tag{A17}$$

while the odd ℓ series starts with

$$I_1^0 \equiv \int_0^z j_1(x)dx = 1 - j_0(z), \tag{A18}$$

a result obtained from Eq. (A16) for $\ell = 1$. Equation (A16) is the analog of Eq. (A5) for the $I_\ell^0(z)$ integrals. Equation (A16) for $\ell > 2$, together with the starting expressions (A17) for the even ℓ values and (A18) for the odd ones, produces the integral $I_\ell^0(z)$ for any value of ℓ and is easily programmable. Again, we shall also give the expression of $I_\ell^0(z)$. The analog of (A9) is

$$I_\ell^0(z) = \frac{(\ell-1)!!}{\ell!!} I_p^0(z) - \frac{(\ell-1)!!}{\ell!!} \times \sum_{\substack{q=1\\ \text{odd}}}^{\ell-1-p} \frac{(\ell-q-1)!!}{(\ell-q)!!}[2(\ell-q)+1)] j_{\ell-q}(z), \tag{A19}$$

valid for $\ell \geqslant 2$, with p as defined above.

APPENDIX B: THE $1s \to 2p_1$ TRANSITION MATRIX ELEMENT FOR THE MULTIPOLAR HAMILTONIAN

The theoretical approach that is presented in this work is concerned with the calculation of matrix elements of atom-radiation interaction, at the level of the multipolar Hamiltonian. The formal theory of the MPH and its connection to the minimal coupling Hamiltonian is presented clearly in Refs. [6,7].

In order to illustrate the applicability of the formulation, here we derive the analytic result for the MPH matrix element of the simplest possible one-photon transition between two circular states, namely, that for the $1s \to 2p_1$ transition in hydrogen. We stress that the result holds for any value of the frequency of the incident radiation and not just for that on resonance with the energy difference $\omega = (E_{2p} - E_{1s})/\hbar$.

For the on-resonance case, Craig and Thirunamachandran [7] obtained the analytic expression for the $1s \to 2p$ matrix element using the well-known full interaction from the MCH $\frac{e}{mc}\vec{\boldsymbol{p}} \cdot \vec{A}(\vec{\boldsymbol{r}},t)$ [7]. They compared the MCH result to that from the EDA. The analytic expression for the ratio of the matrix elements $\langle \mathrm{MCH}\rangle/\langle \mathrm{EDA}\rangle$ is simple (in a.u.):

$$R(1s \to 2p) = \frac{\langle \mathrm{MCH}\rangle}{\langle \mathrm{EDA}\rangle} = \left[1 + \frac{4}{9}\kappa^2\right]^{-2}, \tag{B1}$$

where κ is the photon wave number, with $\kappa = \omega/c$.

As we will show below, the answer for R which is obtained by using the MPH, is the same. In fact, in order for this equality

between the MCH and MPH results to be achieved precisely (it holds only for the on-resonance matrix element), it is necessary (as dictated by the fundamentals of the theory of radiation) to add the contribution of the magnetic field even though, for this case in hydrogen, it is orders of magnitude smaller than that of the electric field.

Since $\ell_1 = m_1 = 0$ and $\ell_2 = m_2 = 1$, only the term with $\ell = 1$ survives in the expansions (3) and (9) for the interaction Hamiltonians. The radial wave function of a hydrogenic circular state has the simple form of a Slater-type orbital, i.e., $r^{\ell} e^{-[Z/(\ell+1)]}$, where Z is the nuclear charge. In our case, $u_{1s} = 2e^{-r}$ and $u_{2p} = \frac{1}{2\sqrt{6}} r e^{-r/2}$.

1. Matrix element of the electric-field operator

Equation (8) gives $\langle Y_0^0|\Theta_1(\theta,\phi)|Y_1^1\rangle = -\frac{1}{\sqrt{6}}$ for the angular term. The integral F_1 in the expression of the time-independent operator $O_E(\kappa,\vec{r})$ defined in Eq. (3) is, according to (A7),

$$3F_1(\kappa r) = \frac{3}{2\kappa}\mathrm{Si}(\kappa r) - \frac{3}{2\kappa} j_1(\kappa r). \tag{B2}$$

Substituting the above expressions in Eq. (3), we obtain

$$\begin{aligned}&\langle 1s|O_E(\kappa,\vec{r})|2p\rangle \\ &= \frac{1}{4\kappa}\int_0^\infty r^3 e^{-(3/2)r}[\mathrm{Si}(\kappa r) - j_1(\kappa r)]\,dr \\ &= \frac{1}{4\lambda}\left(\frac{2}{3}\right)^5 \int_0^\infty x^3 e^{-x}[\mathrm{Si}(\lambda x) - j_1(\lambda x)]\,dx,\end{aligned} \tag{B3}$$

where $\lambda = \frac{2}{3}\kappa$. After integration the final result is

$$\begin{aligned}\langle 1s|O_E(\kappa,\vec{r})|2p\rangle &= \frac{1}{2}\left(\frac{2}{3}\right)^5 \left[\frac{5+8\lambda^2+3\lambda^4}{(1+\lambda^2)^3} + 3\frac{\tan^{-1}(\lambda)}{\lambda}\right] \\ &= \frac{1}{2}\left(\frac{2}{3}\right)^5 \left[\frac{5+3\lambda^2}{(1+\lambda^2)^2} + 3\frac{\tan^{-1}(\lambda)}{\lambda}\right].\end{aligned} \tag{B4}$$

In the case of the long-wavelength approximation, where $\kappa r \sim 0$, Eq. (B2) is reduced to the EDA form

$$3F_1(\kappa r) \approx r. \tag{B5}$$

Thus the EDA version of Eq. (B3) is

$$\langle 1s|O_E(\kappa,\vec{r})|2p\rangle_{\mathrm{EDA}} = \frac{1}{4\lambda}\left(\frac{2}{3}\right)^5 \int_0^\infty x^4 e^{-x} dx = \frac{2^7}{3^5}. \tag{B6}$$

The expression (B6) is also obtained from Eq. (B4) for $\lambda = 0$. Using Eqs. (B4) and (B6), we obtain the ratio

$$\frac{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle}{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle_{\mathrm{EDA}}} = \frac{1}{2^3}\left[\frac{5+3\lambda^2}{(1+\lambda^2)^2} + 3\frac{\tan^{-1}(\lambda)}{\lambda}\right]. \tag{B7}$$

2. Matrix element of the paramagnetic-field operator

Equation (12a) gives $\langle Y_0^0|\Theta_1(\theta,\phi)|Y_1^1\rangle = -\frac{1}{2i\sqrt{6}}$ for the angular term. The integral F_1 in the expression of the time-independent operator $O_B(\kappa,\vec{r})$ defined in Eq. (13) is, according to (A14) and (A17),

$$3F_1(\kappa r) = \frac{3}{(\kappa r)^2}[\mathrm{Si}(\kappa r) - \sin(\kappa r)]. \tag{B8}$$

Thus, for the magnetic field we obtain

$$\begin{aligned}&\langle 1s|O_B(\kappa,\vec{r})|2p\rangle \\ &= -\frac{3}{\sqrt{6}\kappa^2}\int_0^\infty r\, e^{-(3/2)r}[\mathrm{Si}(\kappa r) - \sin(\kappa r)]\,dr \\ &= -\frac{3}{\sqrt{6}}\left(\frac{2}{3}\right)^4 \frac{1}{\lambda^2}\int_0^\infty x e^{-x}[\mathrm{Si}(\lambda x) - \sin(\lambda x)]\,dx.\end{aligned} \tag{B9}$$

Performing the integration, we obtain

$$\langle 1s|O_B(\kappa,\vec{r})|2p\rangle = \frac{4}{3^4\lambda^2}\left\{\lambda\frac{1-\lambda^2}{(1+\lambda^2)^2} - \tan^{-1}(\lambda)\right\}. \tag{B10}$$

Division of Eq. (B10) by the EDA result yields

$$\begin{aligned}&\frac{\langle 1s|O_B(\kappa,\vec{r})|2p\rangle}{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle_{\mathrm{EDA}}} \\ &= \frac{1}{2^5\lambda}\left[3\frac{1-\lambda^2}{(1+\lambda^2)^2} - 3\frac{\tan^{-1}(\lambda)}{\lambda}\right] \\ &= \frac{1}{4\lambda}\left[\frac{1}{(1+\lambda^2)^2} - \frac{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle}{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle_{\mathrm{EDA}}}\right],\end{aligned} \tag{B11}$$

where use of (B7) was made.

3. Matrix element of the full operator

In order to obtain the total matrix element, we add the expression (B11), divided by c, to (B7). Now $c\lambda = \frac{2}{3}\omega$ and

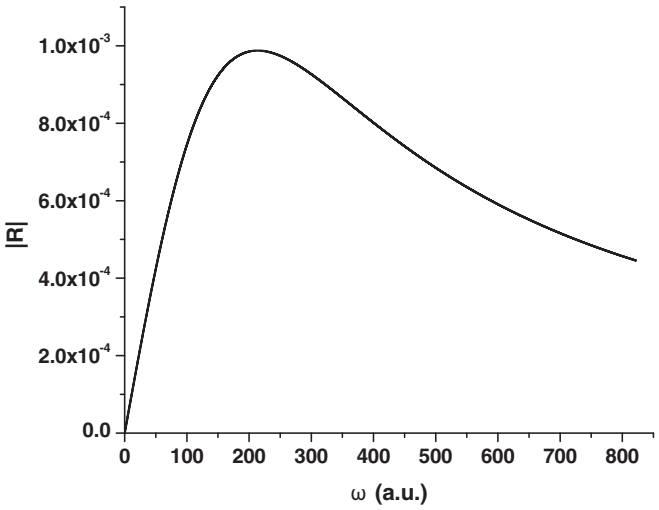

FIG. 7. Absolute value of the ratio R of the matrix element of the paramagnetic field operator to that of the electric one [Eqs. (B11) and (B7)] for the transition between the $1s$ and $2p$ circular states of H, as a function of ω.

$\omega = \frac{3}{8}$ a.u., so $c\lambda = \frac{1}{4}$ a.u. Consequently,

$$\frac{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle + c^{-1}\langle 1s|O_B(\kappa,\vec{r})|2p\rangle}{\langle 1s|O_E(\kappa,\vec{r})|2p\rangle_{\mathrm{EDA}}} = \frac{1}{(1+\lambda^2)^2} \equiv \left[1+\frac{4}{9}\kappa^2\right]^{-2}. \quad \text{(B12)}$$

Equation (B12) is identical to Eq. (B1).

Finally, it is of interest to calculate the ratio R of the matrix element of the paramagnetic field operator to that of the electric one [Eqs. (B11) and (B7)]. The absolute value of the ratio $|R|$ is shown in Fig. 7 as a function of ω; $|R|$ takes its maximum value of 9.88×10^{-4} for $\lambda = 1.04$ a.u. ($\omega = 213.8$ a.u.), a result showing that the electric-field operator is the most significant part of the multipolar interaction Hamiltonian.

The ratio of the matrix elements shown in Eq. (B12) corresponds to nuclear charge $Z = 1$. For the case of $Z \neq 1$ it takes the general form $[1+\frac{4}{9}(\frac{\kappa}{Z})^2]^{-2} = [1+3.328Z^2\times10^{-6}]^{-2}$.

This is so because $\kappa = \omega/c$ scales as Z^2 for the on-resonance case ($\omega = E_{2p} - E_{1s}$). Consequently, apart from relativistic effects on the wave functions, the larger the nuclear charge Z is, the larger the deviation of the full operator matrix elements from its EDA counterpart is.

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