Application of the Sturmian expansion to multiphoton absorption by hydrogen above the ionization threshold

Robin Shakeshaft
Physics Department, University of Southern California, Los Angeles, California 90089-0484
(Received 19 May 1986)

The convergence of the Sturmian expansion of the multiphoton matrix element for hydrogen is accelerated by regularizing, in a convenient way, the outgoing part of the stationary wave of the emergent electron. Some results are presented.

I. INTRODUCTION

Since the Sturmian expansion of the matrix element for multiphoton ionization of hydrogen diverges for positive intermediate energies, it is necessary to invoke some technique to analytically continue from negative to positive energies. However, numerical difficulties persist in all such techniques adopted so far, and have limited the applicability of the Sturmian approach to at most two-photon absorption above threshold.[1-3] In two recent papers[4] I developed further insight into the divergence problems attendant to the Sturmian expansion, and introduced modifications to alleviate these problems. Here I continue the study by resolving the most serious of the remaining numerical difficulties, and report results of calculations of cross sections for multiphoton ionization of ground-state hydrogen with up to three photons absorbed above threshold.

The Sturmian functions $S^k_{nl}(r)=(r\,|\,S^k_{nl})$ are defined by the eigenvalue equation $(T_l+\lambda^k_{nl}V)\,|\,S^k_{nl})=E\,|\,S^k_{nl})$ together with the normalization $(S^k_{n'l}\,|\,V\,|\,S^k_{nl})=\beta^k_{nl}\delta_{n'n}$ and the boundary condition that $S^k_{nl}(r)$ is damped by the factor $\exp(-kr)$ for $r\sim\infty$, where $k=\sqrt{-2E}$. (We use atomic units.) Here T_l is the radial kinetic energy operator and, in coordinate space, $V=-Z/r$. For E real and negative the $|\,S^k_{nl})$ form a complete set in the space L^{l+1}_V of all piecewise continuous functions $f(r)=(r\,|\,f)$ for which $(f\,|\,V\,|\,f)$ is finite and $f(r)/r^{l+1}$ is bounded for $r\sim 0$. We allow E to be complex, $E=|\,E\,|e^{i\theta}$, with $k=|\,k\,|e^{-i\phi}$ and $\phi=(\pi-\theta)/2$. With $g_l(E)=1/(E-T_l-V)$, i.e., the radial Green's operator, the matrix element $(a\,|\,g_l(E)\,|\,b)$ can be expanded in the form[4,5]

$$(a\,|\,g_l(E)\,|\,b)=\sum_{n=l+1}^{\infty}\frac{(a\,|\,S^k_{nl})(S^k_{nl}\,|\,b)}{\beta^k_{nl}(\lambda^k_{nl}-1)}\,, \tag{1.1}$$

where $(a\,|\,b)=\int_0^\infty a(r)b(r)dr$. I argued previously[4] that this expansion converges if $|\,a_\phi)$ and $|\,b_\phi)$ belong to $L^l_{1/V}$, where $(r\,|\,a_\phi)=(re^{i\phi}\,|\,a)$ and $(r\,|\,b_\phi)=(re^{i\phi}\,|\,b)$. Consider the matrix element for two-photon ionization. Thus suppose that $a(r)$ is (r times) the radial wave function of the initial state and that $b(r)$ is (r times) the continuum radial wave function of the emergent electron. While $a(r)$ is exponentially damped, and belongs to $L^l_{1/V}$, $b(r)$ is a stationary wave, consisting of both outgoing and ingoing waves, $b^+(r)$ and $b^-(r)$, respectively. We therefore decompose $b(r)$ as $b^+(r)+b^-(r)$; since the two matrix elements resulting from this decomposition are related to one another,[4] we need only consider $b^+(r)$. For E in the upper-half complex plane ($0<\phi<\pi/2$) both $a_\phi(r)=(re^{i\phi}\,|\,a)$ and $b^+_\phi(r)=(re^{i\phi}\,|\,b^+)$ are exponentially damped. However, $b^+_\phi(r)$ is irregular at the origin, and so does not belong to $L^l_{1/V}$. It is the regularization of $b^+_\phi(r)$ that we examine in Sec. II. Note that while $b^+_\phi(r)$ remains exponentially damped as E approaches the positive real axis (from above) $a_\phi(r)$ does not, and $a(ir)$ does not belong to $L^l_{1/V}$. However, as pointed out earlier,[4] we can approximate $|\,a)$ to arbitrary accuracy by truncating the convergent expansion

$$|\,a)=\sum_{n=l+1}^{\infty}(\beta^\kappa_{nl})^{-1}(S^\kappa_{nl}\,|\,a)V\,|\,S^\kappa_{nl}) \tag{1.2}$$

after a sufficient number of terms; provided we choose κ so that $\mathrm{Re}(\kappa e^{i\phi})>0$ this finite series approximation to $a_\phi(r)$ will be exponentially damped even for $\phi=\pi/2$. It turns out[4] that with this replacement for $|\,a)$, the Sturmian expansion of $(a\,|\,g_l(E)\,|\,b^+)$ converges for real positive E even without regularization of $b^+(r)$. In fact, in our previous work[4] we did not regularize $b^+(r)$. However, the convergence was rather slow and the expansion is an alternating series consisting of large terms which cancel in the sum, so that extended precision is required in the computations. We will see below that these drawbacks are greatly reduced when $b^+(r)$ is regularized.

II. REGULARIZATION OF OUTGOING WAVE

Suppose that P photons are sufficient to ionize the atom. The matrix element $M^{(N)}$ for N-photon absorption ($N\geq P$) from a hydrogenlike ion can be decomposed as $M^{(N)}=M^{+(N)}+M^{-(N)}$ where

$$M^{\pm(N)}=(u^\pm_{\bar{K}\bar{L}}\,|\,rg_{l_{N-1}}(E_{N-1})\cdots rg_{l_P}(E_P)r\,|\,a)\,, \tag{2.1a}$$

$$|\,a)=g_{l_{P-1}}(E_{P-1})r\cdots rg_{l_1}(E_1)r\,|\,u_{\bar{n}\bar{l}})\,. \tag{2.1b}$$

where $|\,u_{\bar{n}\bar{l}})$ represents the initial state of the electron, $|\,u^+_{KL})$ and $|\,u^-_{\bar{K}\bar{L}})$ are the outgoing and ingoing components, respectively, of the state vector of the emergent electron, the E_j are the intermediate energies, and the l_j the intermediate orbital angular momentum quantum

numbers. We have $u^{\pm}_{KL}(r)=N_{KL}W_{\nu,\mu}(2Kr)$, where $W_{\nu,\mu}(z)$ is the irregular Whittaker function, $\nu=Z/K$, and $\mu=L+\frac{1}{2}$; here $K=-i\sqrt{2E_N}$, with E_N the (positive) energy of the emergent electron and L its orbital angular momentum quantum number. The normalization is on the energy scale, with N_{KL} the normalization constant.

We replace $r\,|\,a)$ by a truncated expansion of the form displayed in Eq. (1.2), so that $|\,a_\phi)$ belongs to $L^l_{1/V}$ for $\phi=\pi/2$, where $l=l_P$. For $r\sim 0$ we have[6] (recall we use atomic units)

$$u^{\pm}_{KL}(r)=N_{KL}e^{-Kr}\sum_{m=-L}^{L}b_m r^m+O(r^{L+1}\ln r)\,, \tag{2.2a}$$

$$b_m=\frac{(-1)^{m+L}(2K)^m}{\Gamma(L+1-Z/K)}\frac{(L-m)!}{(L+m)!}(-L-Z/K)_{m+L}\,, \tag{2.2b}$$

and so $r\,|\,u^{\pm}_{KL})$ does not belong to $L^l_{1/V}$, where now $l=l_{N-1}$. [Here $(a)_m$ is the Pochhammer symbol.[6]] We introduce a regularized vector $|\,\bar{u}^{\pm}_{KL})$,

$$|\,\bar{u}^{\pm}_{KL})=|\,u^{\pm}_{KL})-N_{KL}\,|\,\psi)\,, \tag{2.3a}$$

$$(r\,|\,\psi)=e^{-kr}\sum_{m=-L}^{l-2}c_m r^m\,, \tag{2.3b}$$

$$c_m=\sum_{p=0}^{m+L}\frac{(k-K)^{m+L-p}}{(m+L-p)!}b_{p-L}\,, \tag{2.3c}$$

where $k=-i\sqrt{2E_{N-1}}$ and $l=l_{N-1}$. (The reason for choosing the exponent to be k, rather than K, will become apparent shortly. Were I to set $k=K$ I would obtain $c_m=b_m$.) For $r\sim 0$ we have $r\bar{u}^{\pm}_{KL}(r)=O(r^l)$, noting that $l-1\leqq L$, and hence $r\,|\,\bar{u}^{\pm}_{KL})$ belongs to $L^l_{1/V}$. Therefore the matrix element $\bar{M}^{+(N)}$, obtained by replacing $|\,u^{\pm}_{KL})$ by $|\,\bar{u}^{\pm}_{KL})$ in Eq. (2.1a), is expected to have a rapidly convergent Sturmian expansion.

We must now take into account the subtraction term $|\,\psi)$. We introduce $|\,\chi)=g_l(E_{N-1})r\,|\,\psi)$. With E_{N-1} on the upper edge of the positive real axis, $(r\,|\,\chi)$ is an outgoing wave and behaves as r^{3-L} for $r\sim 0$. (This can be seen by expressing $g_l(E)$ in coordinate space in the form of the product of the regular and irregular Whittaker functions.) Now $(r\,|\,\chi)$ satisfies the differential equation

$$\left[\frac{1}{2}\frac{d}{dr^2}-\frac{l(l+1)}{2r^2}+\frac{Z}{r}-\frac{1}{2}k^2\right]\chi(r)=r\psi(r)\,. \tag{2.4}$$

To any particular solution of this equation we can add $\alpha W_{Z/k,l+1/2}(2kr)$, this being an outgoing wave solution to the homogeneous equation. The constant α is determined by the behavior of $\chi(r)$ at $r\sim 0$. To find a particular solution we write $\chi(r)=e^{-kr}f(r)$; we have

$$\left[\frac{1}{2}\frac{d^2}{dr^2}-k\frac{d}{dr}-\frac{l(l+1)}{2r^2}+\frac{Z}{r}\right]f(r)=\sum_{m=-L}^{l-2}c_m r^{m+1}\,. \tag{2.5}$$

The absence of a constant term on the left of this equation is a consequence of choosing the exponent in $\psi(r)$ to be k, rather than K, and it allows us to write the particular solution in the form

$$f(r)=\sum_{m=-l-1}^{l-1}f_m r^{m+1}\,. \tag{2.6a}$$

Substituting this form into Eq. (2.5) we obtain a recurrence relation for the coefficients f_m,

$$\tfrac{1}{2}[m(m+1)-l(l+1)]f_m+(-mk+Z)f_{m-1}=c_{m-2}\,. \tag{2.6b}$$

This recurrence relation can be started at $m=l$. Note that $c_{l-2}\neq 0$ and that f_{l-1} is uniquely defined. Also, since $c_m=0$ for $m>l-2$ and $m<-L$ (and hence $m<-l-1$) we necessarily have $f_m=0$ for $m>l-1$ and $m<-l-1$.

The complete solution is

$$\chi(r)=\alpha W_{Z/k,l+1/2}(2kr)+e^{-kr}\sum_{m=-l-1}^{l-1}f_m r^{m+1}\,. \tag{2.7a}$$

We must choose α so that the terms labeled by $m=-l-1$ through $1-L$ cancel with the corresponding terms in the Whittaker function so that $\chi(r)$ behaves as r^{3-L} for $r\sim 0$. In fact, α is fixed by the requirement that just the $m=-l-1$ term cancels,

$$\alpha=-[(2k)^l/(2l)!]\Gamma(l+1-Z/k)f_{-l-1}\,. \tag{2.7b}$$

That further terms cancel with this choice of α, to give the correct behavior of $\chi(r)$ for $r\sim 0$, may be verified from the recurrence relations (2.6b) noting that $c_m=0$ for $m<-L$.

It follows that[7]

$$M^{+(N)}=\bar{M}^{+(N)}+(\alpha N_{KL}/N_{kl})M^{+(N-1)}+N_{KL}\sum_{m=-l-1}^{l-1}f_m F^{(N-1)}_m\,, \tag{2.8a}$$

$$F^{(N-1)}_m=(r^{m+1}e^{-kr}\,|\,rg_{l_{N-2}}(E_{N-2})\cdots r\,|\,a)\,. \tag{2.8b}$$

This relationship expresses $M^{+(N)}$ in terms of $\bar{M}^{+(N)}$, which is easily calculated, and quantities related to an $(N-1)$-photon process. The matrix elements $M^{+(N)}$ can therefore be calculated recursively down to $N=P+1$. It is straightforward to calculate the $F^{(N-1)}_m$ recursively using the same procedure. Thus we introduce

$$\bar{F}^{(N-1)}_m=(\bar{\psi}_m\,|\,rg_{l_{N-2}}(E_{N-2})\cdots r\,|\,a)\,, \tag{2.9a}$$

$$(r\,|\,\bar{\psi}_m)=r^{m+1}e^{-kr}-e^{-k'r}\sum_{m'=m}^{l'-2}d_{mm'}r^{m'+1}\,, \tag{2.9b}$$

$$d_{mm'}=(k'-k)^{m'-m}/(m'-m)!\,, \tag{2.9c}$$

where $k'=-i\sqrt{2E_{N-2}}$ and $l'=l_{N-2}$. We have that $r\bar{\psi}_m(r)$ behaves as $r^{l'}$ for $r'\sim 0$ and it therefore belongs to $L^{l'}_{1/V}$ so that $\bar{F}^{(N-1)}_m$ can be easily calculated. Following the same procedure as above, we find that

$$F^{(N-1)}_m=\bar{F}^{(N-1)}_m+(\alpha'_m/N_{k'l'})M^{+(N-2)}+\sum_{m'=-l'-1}^{l'-1}g_{mm'}F^{(N-2)}\,, \tag{2.10}$$

where $\alpha'_m=-[(2k')^{l'}/(2l')!]\Gamma(l'+1-Z/k')g_{m,-l'-1}$ and where the $g_{mm'}$ satisfy a recurrence relation (in m') similar to that satisfied by the f_m. Knowledge of $M^{+(P)}$ and

the $F_m^{(P)}$, which are easily calculated, therefore allows us to generate all the $M^{+(N)}$.

We finally require $M^{(N)}$ of course. This can be obtained from $M^{+(N)}$ through the relation[4,8]

$$M^{(N)}=2\,\mathrm{Re}[M^{+(N)}]-2\pi i\sum_{i=1}^{N-P}J_i^{(N)}M^{(N-i)}\,, \tag{2.11a}$$

$$J_i^{(N)}=(u_{KL}^{+}\,|\,rg_{l_{N-1}}(E_{N-1})\cdots \times g_{l_{N-i+1}}(E_{N-i+1})r\,|\,u_{k_{N-i},l_{N-i}})^{*}\,, \tag{2.11b}$$

$$J_1^{(N)}=(u_{KL}^{+}\,|\,r\,|\,u_{k_{N-1},l_{N-1}})^{*}\,, \tag{2.11c}$$

where $k_j=-i\sqrt{2E_j}$ and where the stationary wave vector $|\,u_{k_jl_j}\rangle$ represents a photoelectron emerging with energy E_j. The matrix element $J_i^{(N)}$ can be evaluated by first using the expansion[4]

$$|\,u_{k_j}\rangle=e^{\xi r}\sum_{n=l_j+1}^{\infty}(\beta_{nl}^{\kappa})^{-1}(S_{nl_j}^{\kappa}\,|\,Ve^{-\xi r}\,|\,u_{k_j})S_{nl_j}^{\kappa}(r)\,, \tag{2.12}$$

where ξ and κ are restricted by the conditions listed in Eqs. (2.17) of Ref. 4(b). Provided that these conditions are satisfied, we obtain a convergent expansion of $(u_{KL}^{+}\,|\,r\cdots rg_{l_{j+1}}(E_{j+1})r\,|\,u_{k_jl_j})$ by truncating the expansion of Eq. (2.12) and using the Sturmian expansions of the Green's functions together with the procedure, outlined above, for regularizing $|\,u_{KL}^{+}\rangle$.

III. APPLICATION

The exponent κ which appears in the truncated expansion of $|\,a\rangle$—see Eqs. (1.2) and (2.1b)—was chosen to have the form $\kappa=\gamma k_{P-1}+\delta k_P$, with γ and δ in the range [0,1]. The coefficients γ and δ were, in fact, chosen empirically at each wavelength to achieve good convergence while keeping the number of terms in the expansion of $|\,a\rangle$ small (typically ten).

The exponents ξ and κ in the truncated expansion of $|\,u_{k_j}\rangle$—see Eq. (2.12)—were chosen to have the form

$$\xi=\zeta(k_j+k_{j+1})\,,\quad \kappa=\eta\xi$$

with ζ and η real and positive. Note that here ξ and κ are pure imaginary (and differ from the choice made in Ref. 4). In most cases we chose $\zeta=\frac{1}{2}$ so that both inequalities (2.17a) and (2.17c) in Ref. 4(b) were satisfied. The coefficient η can be chosen so that $\kappa-\xi=k_{j+1}$; this particular choice results in a considerable simplification in the evaluation of the integral

$$I_{n'n}=\int_0^{\infty}dr\,e^{\xi r}S_{nl_j}^{\kappa}(r)S_{n'l_{j+1}}^{k_{j+1}}(r)\,,$$

and in fact leads to $I_{n'n}$ vanishing for $n'>n+2$. However, it is not always advantageous to choose $\kappa-\xi=k_{j+1}$ since, with this choice, $|\,I_{n'n}\,|$ can for some wavelengths become very large for $n\gg 1$, and this results in extensive cancellation elsewhere in the sum. [The principal source of cancellation throughout the calculation is the subtraction indicated in Eq. (2.3a), which arises in the regularization process.] Typically we chose η to be between 1.5 and 3, which in most cases limited $I_{n'n}$ to reasonable values; note that $I_{n'n}$ decreases with increasing η and is zero for $\eta\sim\infty$. However, occasionally, in order to restrict the magnitude of $I_{n'n}$, it was necessary to choose $\zeta>\frac{1}{2}$; with larger values of ζ, inequality (2.17a) in Ref. 4(b) is satisfied by a wider margin but inequality (2.17c) is then violated, and this slows down (but does not destroy) the convergence of the Sturmian expansions of the Green's functions in the matrix elements $J_i^{(N)}$

In Tables I and II I present results of calculations of the generalized cross section $\hat{\sigma}_N$ for N-photon ionization of ground-state hydrogen by circularly polarized light. All computations were done without using extended precision (only 16 significant figures were retained in the computations). The convergence of all intermediate sums was rather fast; in most cases it was unnecessary to retain more than 30 terms in any sum, although in the evaluation of the matrix elements $J_i^{(N)}$ it was sometimes necessary to include up to 50 terms in some sums. The results for $\hat{\sigma}_3$ in Table I agree (to the two figures presented) with those of Klarsfeld and Maquet[2] and Aymar and Crance,[9] where comparison is possible. At high energies ($\lambda<500$ Å) or near threshold (e.g., $\lambda\sim900$ Å) it is necessary, for $N-P=3$, to use extended precision in the computation; this increases the computation time significantly. For $N-P\geq 4$ or $N>P>2$ it is necessary to use extended precision at all wavelengths. We have not performed calculations for ionization of *excited* states, but we do not anticipate difficulties for $P=1$ and $N\leq 2$ or perhaps 3, and for excited states with principal quantum numbers $\lesssim 10$.

TABLE I. Generalized cross sections for one-, two-, three-, and four-photon ionization of ground-state hydrogen by circularly polarized light at various wavelengths λ. Units of $\hat{\sigma}_N$ are $\mathrm{cm}^{2N}\mathrm{sec}^{N-1}$. Square brackets indicate powers of ten, e.g., $1[5]=1\times10^5$.

λ (Å)	500	600	700	800
$\hat{\sigma}_1$	1.2[−18]	2.0[−18]	3.1[−18]	4.4[−18]
$\hat{\sigma}_2$	3.4[−53]	9.2[−53]	2.2[−52]	4.6[−52]
$\hat{\sigma}_3$	6.4[−88]	2.6[−87]	8.7[−87]	2.5[−86]
$\hat{\sigma}_4$	1.1[−122]	6.2[−122]	2.9[−121]	1.1[−120]

TABLE II. Generalized cross sections (in units of $\mathrm{cm}^{2N}\mathrm{sec}^{N-1}$) for two-, three-, four-, and five-photon ionization of ground-state hydrogen at wavelengths where the minimum number of photons required to ionize the atom is two. Square brackets indicate powers of ten, e.g., $1[5]=1\times10^5$.

λ (Å)	1200	1300	1400
$\hat{\sigma}_2$	1.3[−49]	2.9[−50]	1.8[−50]
$\hat{\sigma}_3$	1.4[−83]	5.6[−84]	4.8[−84]
$\hat{\sigma}_4$	1.3[−117]	6.8[−118]	7.4[−118]
$\hat{\sigma}_5$	1.1[−151]	7.9[−152]	1.1[−151]

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Mark Edwards for checking some of the results presented here. This work was supported by the National Science Foundation, Grant No. PHY-8512495.

[1]E. Karule, J. Phys. B **11**, 441 (1978); B **18**, 2207 (1985).

[2]S. Klarsfeld and A. Maquet, Phys. Lett. **73A**, 100 (1979); **78A**, 40 (1980).

[3]A. G. Fainshtein, N. L. Manakov, and S. I. Marmo, Phys. Lett. **104A**, 347 (1980).

[4](a) R. Shakeshaft, J. Phys. B **18**, L611 (1985); (b) Phys. Rev. A **34**, 244 (1986).

[5]L. C. Hostler, J. Math. Phys. **11**, 2966 (1970).

[6]M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970), chap. 13.

[7]Note that $(\psi \mid rg_l(E)r \mid \phi)=(\phi \mid rg_l(E)r \mid \psi)$ since here $(r \mid \phi)$ is either a damped wave or an outgoing wave; in the latter case we can, in principle, rotate the integration contour into the upper-half complex r plane to ensure that the integrand is damped for $\mid r \mid \sim \infty$.

[8]The recurrence relations of Eqs. (2.11) have been usefully applied to the treatment of multiphoton ionization of alkali atoms; see M. Edwards, X. Tang, P. Lambropoulos, and R. Shakeshaft, Phys. Rev. A **33**, 4444 (1986).

[9]M. Aymar and M. Crance, J. Phys. B **14**, 3585 (1981).