Near-threshold photoabsorption cross sections for nonhydrogenic ions

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Nonhydrogenic photoabsorption cross sections near threshold are well approximated by radial dipole-matrix elements between phase-shift-modulated regular and irregular Coulomb continuum and quantum-defect bound-state wave functions. Results based upon numerical quadratures are inaccurate for high-Rydberg transitions, while previous analytical formulas are difficult to evaluate near threshold. A simple analytic algorithm for the near-threshold region based on the analytic properties of the Coulomb functions in the complex energy plane is presented.

I. INTRODUCTION

The computation of atomic photoabsorption cross sections and multiphoton excitations require a number of electric dipole-matrix elements between nonhydrogenic bound and continuum states. Expressions employing quantum-defect wave functions[1] afford a good approximation because the major contribution to the radial matrix element occurs outside of the core region. There the single-electron potential is essentially Coulombic and the wave functions are well approximated by certain linear combinations of regular and irregular Coulomb functions.

Using the Coulomb approximation, Burgess and Seaton[2] obtained matrix elements by numerical quadrature. These were fix to simply parametrized forms. The tabulated parameters, as extended by Peach,[3] are extremely useful for transitions from low principle and orbital quantum number states. For high Rydberg excitations the numerical quadratures are more difficult to perform accurately and the simple prescription for fitting the results breaks down.

As shown by McGuire,[4] and also by Dy and VanRegemorter,[5] analytic expressions for the matrix elements are also available. These offer the advantage of being fully general and equally applicable to high Rydberg transitions. However, the resulting hypergeometric functions are difficult to evaluate at threshold, and for high Rydberg excitations it is precisely in the region near threshold where photoabsorption cross sections vary dramatically.

Tó supplement the results of Dy and VanRegemorter, we present in this paper analytic expressions for the photoabsorption cross section valid near threshold. They are based on the structure of Coulomb functions in the entire (complex) energy plane as discussed by Humblet.[6] Simple, efficient algorithms for its numerical evaluation are presented.

II. BOUND-STATE WAVE FUNCTION

Unit-normalized bound wave functions, according to the quantum-defect method, are given by

$$P_{\nu l}(r)=Z^{1/2}K(\nu,l)W_{\nu,l+1/2}(2Zr/\nu)\ . \tag{1}$$

W is the standard Whittaker function,[7] Z is the net charge of the parent ion, and the noninteger effective principle quantum number ν is determined from the eigenvalue as

$$E=-Z^2/\nu^2\ . \tag{2}$$

We assume E is in Rydbergs and r is in Bohr. The normalization factor is

$$N(\nu,l)=[\nu^2\Gamma(\nu+l+1)\Gamma(\nu-l)]^{-1/2}\ . \tag{3}$$

For calculational purposes we shall employ a truncated asymptotic expansion for the Whittaker function

$$W_{\nu,l+1/2}\left[2\frac{Zr}{\nu}\right]=\left[2\frac{Zr}{\nu}\right]^{\nu}e^{-Zr/\nu}\sum_{t=0}^{t_F}b_t(\nu,l)/(Zr)^t\ . \tag{4}$$

The coefficients satisfy a simple recursion relation

$$b_t=\frac{\nu}{2t}[l(l+1)-(\nu-t)(\nu-t+1)]b_{t-1}\ ,\quad b_0=1\ . \tag{5}$$

The maximum index t_F is the integer satisfying

$$\nu-l-1\le t_F<\nu-l \tag{6}$$

in oder that the wave function remain finite at the origin and grow at least as fast as r^1, a small relaxation of strictly required boundary conditions.

III. CONTINUUM WAVE FUNCTION

The approximate energy normalized free radial wave function is taken as

$$\left[\frac{2}{\pi k}\right]^{1/2}[F_{\eta'l'}(r)\cos\pi\mu'-G_{\eta'l'}(r)\sin\pi\mu']\ , \tag{7}$$

where μ' is the continuum generalization of the quantum effect, F and G are the regular and irregular Coulomb continuum wave functions of energy

$$E\equiv K^2=\frac{Z^2}{\eta^2}\ , \tag{8}$$

defined by their asymptotic behavior at infinity

$$\begin{Bmatrix} F \\ G \end{Bmatrix} \sim \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} \left[Kr - \eta \ln Kr - \frac{l\pi}{2} + \sigma_l \right] \tag{9}$$

and the Coulomb phase shift σ_l satisfies the equation

$$e^{2i\sigma_l} = \Gamma(l+1+i\eta)/\Gamma(l+1-i\eta) \ . \tag{10}$$

By convention we take η to be negative for attractive potentials.

Following the notation of Yost *et al.*,[8] we may express the regular and irregular functions in terms of the Whittaker function and its complex conjugate as

$$F = \tfrac{1}{2}(H^* + H) \ , \quad G = \tfrac{1}{2}(H^* - H) \tag{11}$$

where

$$H_{\eta,l} = \left[\frac{\Gamma(l+1+i\eta)}{\Gamma(l+1-i\eta} \right]^{1/2} e^{+\pi\eta/2} e^{-i\pi/2(l+1)} \times W_{-i\eta,(l+1/2)}(-2iKr) \ . \tag{12}$$

IV. TRANSITION INTEGRAL

The dipole-matrix element between the bound-state wave function, Eq. (1), and the continuum wave function, Eq. (7), can be obtained from the real and imaginary parts of the radial integral

$$\bar{R} = \int_0^\infty dr \, P_{\nu l} r H_{\eta l'} \ . \tag{13}$$

The lower limit of the integrand is finite due to the truncation of the bound-state expansion and the integral can be written more explicitly as

$$\bar{R} = \frac{N(\nu,l)}{Z^2} (2/\nu)^\nu \sqrt{2/\pi} \times \left[\frac{(\eta')^{2l'+1} e^{-\pi\eta'}}{\Gamma(l'+1+i\eta')\Gamma(l'+1-i\eta')} \right]^{1/2} \times \frac{(-i)}{2^{l'}} \sum_t b_t I_t \ , \tag{14}$$

where

$$I_t \equiv \frac{\Gamma(l'+1-i\eta)}{(i\eta'/2)^{l'}} \int_0^\infty d\rho \, \rho^{\nu+1-t} e^{-\rho/\nu} \times W_{i\eta',l'+1/2}(2\rho/i\eta') \tag{15}$$

can be integrated analytically to give

$$I_t = \left[\frac{i\eta'\nu}{\nu+i\eta'} \right]^a \left[\frac{i\eta'}{2} \right]^{-m} \frac{\Gamma(a)\Gamma(b)\Gamma(a-m)}{\Gamma(a+b-m)} \times {}_2F_1(a,b,a+b-m,z) \ . \tag{16}$$

For notational convenience we have introduced the variables

$$\begin{aligned} a &= \nu + l' + 3 - t \ , \\ b &= l' + 1 - i\eta' \ , \\ m &= 2l' + 1 \ , \\ x &= -\frac{\nu - i\eta'}{\nu + i\eta'} \ . \end{aligned} \tag{17}$$

By using a hypergeometric connection formula[9] Eqs. (14)–(16) can be shown to be equal to the expression presented by Dy and VanRegemorter.[10] For values of η' not too large the hypergeometric function may be evaluated using the rational (complex) polynomial approximation of Luke[11] (see Appendix). As written here the expression is machine indeterminant at threshold energy (η' infinite) and algorithms for the direct evaluation of the hypergeometric function break down in this regime. However, in this limit the argument of the ${}_2F_1$ function approaches unity as the inverse of η, and using a linear transformation formula[12] results in an ascending power series that can be analytically regrouped so as to remain finite at threshold. The resulting expression is

$$I_t = (-2)^m (1 - iK\nu/Z)^m \left[\frac{\nu}{1-iK\nu/Z} \right]^a \Gamma(a)\Gamma(a-m)\xi_{-m(0)} \frac{(-1)^{m+1}}{\Gamma(a-m)} \times \sum_{r=0}^\infty \frac{(a)_r}{r!(r+m)!} (-2\nu)^r \xi_r(0) \left[\ln(-2\nu) - \Psi(1+r) - \Psi(1+r+m) + \Psi(a+r) + \Psi(b+r) + \ln \frac{iK}{Z - i\nu K} \right] , \tag{18}$$

where we have defined the finite product

$$\xi_t(J) \equiv \prod_{s=1}^{t} \frac{Z + iK(l'+1-J+s)}{Z - iK\nu} \quad \text{for } t \text{ positive} \ . \tag{19}$$

This finite product is to be interpreted as unity for index 0. For negative index $-j$ the product is taken over $s = 1, -2, \ldots, -j$. Note that at threshold Eq. (19) reduces to unity. Also, the divergence of the logarithm containing k is canceled by the last Ψ function (however, the result has only an asymptotic expansion about $K = 0$). As a consequence, the integral is proportional to the irregular confluent geometric function

$$U(a,m+1,-2\nu)\ . \tag{20}$$

For high Rydberg states the argument is a large negative number, and the straightforward summation of the series is extremely slow to converge. Furthermore, the alternating signs in the series can result in severe cancellation errors. At threshold one has recourse to known asymptotic forms of the confluent hypergeometric function, but this is no longer the case off threshold. For this reason we turn to the alternative approach presented in Sec. III.

V. ANALYTIC EXPRESSIONS NEAR THRESHOLD

Using the results of Humblet,[6] the regular and irregular Coulomb continuum wave functions may be factorized, separating pieces which have no convergent Mclaurin series expansion in energy from those pieces which are entire in energy. The latter may be expressed in terms of an expansion in regular and irregular Bessel functions. A simple algorithm exists for the computation of the expansion coefficients, and we may analytically integrate term by term to obtain a convergent energy power series for the dipole radial matrix elements.

The regular Coulomb wave function is expressed as

$$F=\Gamma(2l+2)C_l(\eta)(Kr)^{l+1}\Phi_l\ , \tag{21}$$

where the Gamow factor C_l is defined by (η positive for repulsion)

$$C_l(\eta)=\frac{2^l e^{-\pi\eta/2}}{\Gamma(2l+2)}[\Gamma(l+1-i\eta)\Gamma(l+1+i\eta)]^{1/2} \tag{22}$$

and the piece entire in energy is expanded as

$$\Phi_l=\sum_{\mu=0}^{\infty}(-1)^{\mu}\eta^{-2\mu}J_{\mu}^{(l)}(Zr)\ , \tag{23}$$

where the generalized Bessel function is defined in terms of common Bessel functions by the finite sum

$$J_{\mu}^{(l)}(Zr)=\frac{1}{12^{\mu}\mu!}(2Zr)^{2\mu}\times\sum_{\lambda=0}^{\mu}\alpha_{\mu\lambda}^{(l)}(2Zr)^{-[2l+1+\mu+\lambda]/2}\times J_{2l+1+\mu+\lambda}(2\sqrt{2Zr}\ )\ . \tag{24}$$

The coefficients needed to calculate the generalized Bessel function are given by a simple three-term recursion relation

$$\alpha_{\mu\lambda}^{l}=\frac{3\mu}{3\mu-\lambda}\alpha_{\mu-1,\lambda}^{(l)}+\frac{(2l-\mu+\lambda)(\mu-\lambda+1)}{3\mu-\lambda}\alpha_{\mu,\lambda-1}^{(l)}\ , \tag{25}$$

with the starting condition

$$\alpha_{00}^{(l)}=\alpha_{10}^{(l)}=1\ \ \alpha_{11}^{(l)}=l\ . \tag{26}$$

The irregular Coulomb wave function is factorized as ($\eta'=-\eta$ is positive for attraction)

$$G=(2\eta)^{2l+1}(Kr)^{l+1}\frac{1}{C_l(\eta)\Gamma(2l+2)}\times[h(\eta')P_l(\eta')\Phi_l+P_l(\eta')\Theta_l]\ . \tag{27}$$

The function P_l is a simple polynomial in energy,

$$P_l(\eta)=(1-l^2\eta^{-2})[1+(l-1)^2\eta^{-2}]\cdots(1+\eta^{-2}) \tag{28}$$

(unity for $l=0$) and Φ_l is the function entire in energy defined above. Note that the function

$$h(\eta)=\tfrac{1}{2}[\Psi(1-i\eta)+\Psi(1+i\eta)]-\ln\eta \tag{29}$$

is not single valued and has an essential singularity at $K=0$. By its presence any expansion of the irregular Coulomb wave function as a whole must be asymptotic. By isolating its presence the remaining functions in r are entire in energy. The remaining function may be expanded as

$$\Theta_l=\sum_{\mu=0}^{\infty}(-1)^{\mu}(\eta)^{-2\mu}\left[\pi Y_{\mu}^{(l)}(Zr)-\sum_{m=0}^{\mu}(-1)^m b_m J_{\mu-m}^{(l)}(Zr)\right]\ , \tag{30}$$

where the generalized irregular Bessel function is defined analogously to Eq. (24) by replacing regular by irregular common Bessel functions. The coefficients b_m are given in terms of Bernoulli numbers

$$b_0=0\ ,\ \ b_m=|B_{2m}|/2m \tag{31}$$

and arise in connection with the asymptotic expansion of Eq. (29). Note that although they grow quite rapidly with increasing order, they enter here only through a finite sum.

Upon integrating over the bound-state wave function [Eqs. (1)–(6)] one can write the dipole radial matrix elements for the regular and irregular Coulomb continuum wave function as

$$\bar{R}_{\rm reg}=AD\sum_{\mu=0}^{\infty}\left[-\frac{4\nu^2}{\eta^2}\right]^{\mu}\sum_{t=0}\frac{b_t}{\nu^t}J_{\mu,t}^{l'}\ , \tag{32}$$

$$\bar{R}_{\rm irr}=-2^{2l'+1}\frac{A}{D}\sum_{\mu=0}^{\infty}\left[-\frac{4\nu^2}{\eta^2}\right]^{\mu}P_{l'}(\eta')\sum_{t=0}\frac{b_t}{\nu^t}\left[\pi Y_{\mu,t}^{l'}+h(\eta')J_{\mu,t}^{l'}-\sum_{0}^{\mu}(-1)^s\frac{b_s}{(2\nu)^{2s}}J_{\mu-s,t}^{l'}\right]\ , \tag{33}$$

respectively. For notational convenience we have defined the quantities

$$A = 2^{\nu}\nu^{l'+3}\frac{N(\nu,l)}{Z^2}\sqrt{2/\pi} \tag{34}$$

and

$$D = \frac{\Gamma(2l'+2)C_{l'}(\eta')}{[(\eta')^{2l'+1}]^{1/2}} . \tag{35}$$

The quantity $J^l_{\mu,t}$ is defined by the integral over the regular generalized Bessel function [Eq. (24)]

$$J^l_{\mu,t} = \frac{1}{(2\nu)^{2\mu}}\int_0^{\infty} dx\, e^{-x}x^{\nu-t+l+2}J^{(l)}_{\mu}(2\sqrt{2\nu x}) . \tag{36}$$

The quantity $Y^l_{\mu,t}$ is the integral defined analogously to Eq. (36) but involving the irregular generalized Bessel function.

Equations (32) and (33) are the main result of this section. The utility of using such an expression for evaluating dipole matrix elements lies in the ability to simply and efficiently calculate $J^l_{\mu,t}$ and $Y^l_{\mu,t}$ for all indices μ,t needed in the summations. To demonstrate this we proceed as follows.

The integral $Y^l_{\mu,t}$ can be found in Gradshteyn and Ryzhik[13] or evaluated from the standard definition of the irregular Bessel function as a L-Hospital limit of regular Bessel functions and known Laplace transforms of regular Bessel functions.[14] (The result in McGuire's paper[15] is in error.) However, the expression obtained is undefined for an integer (bound-state) principle quantum number without a cancellation and limiting procedure. To obtain an analytic form explicitly finite for all ν one must employ connection formulas for the confluent hypergeometric functions.[16] One obtains

$$Y^l_{\mu,t} = \frac{\Gamma(l+1+\kappa)}{12^{\mu}\mu!}\sum_{\lambda=0}^{\mu}\alpha^{(l)}_{\mu,\lambda}\left[-i\frac{{}_1F_1(l+1+\kappa,2l+2+\rho,-2\nu)}{\Gamma(2l+2+\rho)} + \frac{(-1)^{2l+2+\rho}}{\pi}\Gamma(\kappa-l-\rho)U(l+1+\kappa,2l+2+\rho,-2\nu)\right] , \tag{37}$$

where for notational convenience we have defined

$$\kappa \equiv \nu - t + 2 + 2\mu , \quad \rho \equiv \mu + \lambda . \tag{38}$$

Note that the imaginary part is implicitly cancelled out.

The quantity $J^l_{\mu,t}$ can also be evaluated analytically[14] to yield

$$J^l_{\mu t} = \frac{\Gamma(l+1+\kappa)}{12^{\mu}\mu!} \times \sum_{\lambda=0}^{\mu}\alpha^{(l)}_{\mu\lambda}\frac{{}_1F_1(l+1+\kappa,2l+2+\rho,-2\nu)}{\Gamma(2l+2+\rho)} . \tag{39}$$

Note that both $J^l_{\mu,t}$ and $Y^l_{\mu,t}$ can be obtained solely in terms of the real and imaginary parts of the complex irregular confluent hypergeometric function

$$g(x,y) \equiv \frac{(-1)^y}{\pi}\Gamma(1+x-y)U(x,y,-2\nu) \tag{40}$$

and that all terms required for each sum that occurs in Eqs. (32) and (33), (37) and (39) can be obtained from the simple recursion relations

$$\begin{aligned} g(x+2,y) &= [(2x+2-y-2\nu)g(x+1,y) \\ &\quad -(1+x-y)g(x,y)]/(x+1) , \\ g(x+1,y+1) &= [g(x+1,y)-g(x,y)]/(-2\nu) . \end{aligned} \tag{41}$$

The calculational procedure is to start with values $g(x_{\min},y_{\min})$ and $g(x_{\min}+1,y_{\min})$ and recursively compute the matrix of values $g(x_{\min}+j,y_{\min}+i)$ for all i up to $2u_{\max},u_{\max}$, the maximum term of the Mclaurin expansion in energy to be computed. Only indices j greater than i are needed, and $j_{\max}$ is limited by the number of terms retained in the expansion of the bound-state wave function plus $i_{\max}$. To limit cancellation errors the finite sums are computed using a nesting algorithm.

Essentially only two hypergeometric function evaluations are needed to generate matrix elements for a range of energies. These may be calculated rapidly using the ascending-series representation,[17] even in double-precision arithmetic, by employing certain expansions for the inverse of the Γ function[18] and rational polynomial approximations for the Ψ function.[19]

TABLE I. Five-term expansion for the 12P-to-S continuum dipole radial matrix element.

$X=(nk/z)^2$	Imaginary [Eq. (13)]	Real [Eq. (13)]	Burgess[a]
0.0	−101.152	125.283	125.283
0.005	−100.315	124.246	124.247
0.010	−99.488	123.222	123.223
0.020	−97.869	121.214	121.213
0.040	−94.754	117.350	117.350
0.080	−88.984	110.185	110.184
0.160	−79.046	97.809	97.771
0.320	−64.692	79.767	78.717
0.640	−68.102	81.254	54.589

[a]Reference 2.

VI. RESULTS

By setting the effective principle quantum number to an integer, the method outlined in Sec. V can be tested directly. The truncated expansion of the bound state reduces exactly to a hydrogenic wave function, and the real part of the matrix element [Eq. (13)], that is, the dipole-matrix element with the regular Coulomb continuum wave function equals hydrogenic values computed by the method of Burgess.[20] Table I presents values for the transition $12P$ to the continuum S state for the selected energies

$$X = n^2K^2/z^2$$

given directly in Burgess's paper. We list the real and imaginary parts of Eq. (13) obtained by our method (after multiplying by $\sqrt{\pi/2}$ to convert to the continuum wave function normalization of Burgess), and the real part is compared directly to the values given by Burgess. Results for the present method were calculated by summing terms 0 to $\mu=4$ [see Eqs. (23) and (30)]. The results agree extremely well for near threshold values

$$X < \tfrac{1}{3} .$$

Although the expansions are [Eqs. (23) and (30)] absolutely convergent for all energies, the series for the dipole-matrix element converges extremely slowly outside this region. Table II appends the results for the last three values of Table I upon extending the summation to terms $\mu=7$.

Instead, for $X \geq \frac{1}{3}$, the analytic results of Dy and Van-Regemorter,[5] should be used. In that region the hypergeometric function of their Eq. (15) can be brought to a form which is an absolutely convergent power series (see the Appendix). A very fast evaluation is afforded by Luke's algorithm,[11] which analytically continues results into the region $X < \frac{1}{3}$. Table II presents values using the Luke algorithm including some values for $X < \frac{1}{3}$.

VII. CONCLUSION

Algorithms for computing bound-free dipole-matrix elements using a quantum-defect wave function (i.e., noninteger principle quantum number n) were presented for the near-threshold region, $n^2K^2/Z^2 < \frac{1}{3}$, and the high-energy region, $n^2K^2/Z^2 > \frac{1}{3}$. The near-threshold algorithm is particularly efficient because energy-independent coefficients are employed for repeated calculations at differing energies. The high-energy algorithm employs an efficient accurate rational polynomial approximation to the Kummer hypergeometric function which analytically continues results into the near-threshold region. Because of their speed, accuracy, and generality these algorithms are ideally suited for calculations which require large amounts of photoabsorption data from Rydberg like states.

TABLE II. Eight-term expansion for the $12P$-to-S continuum dipole radial matrix element.

$X=(nK/z)^2$	Imaginary [Eq. (13)]	Real [Eq. (13)]	Burgess[a]
0.160	79.013	97.771	97.771
0.320	63.716	78.673	78.717
0.640	35.897	45.705	54.589

[a]Reference 2.

TABLE III. High-energy results for the $12P$-to-S continuum dipole radial matrix element.

X	Imaginary [Eq. (13)]	Real [Eq. (13)]	Burgess[a]
0.160	−78.358 44	97.287 51	97.771
0.320	−63.758 18	78.716 39	78.717
0.640	−44.509 81	54.588 79	54.589
1.280	−25.845 20	31.185 79	31.186
2.560	−12.424 32	14.508 89	14.509
5.120	−5.111 974	5.649 164	5.6492
10.240	−1.888 483	1.924 000	1.9240
20.480	−0.651 760 6	0.594 566 6	0.594 56

[a]Reference 2.

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APPENDIX

Using a hypergeometric connection formula[10] Eq. (15) of the text is brought to the form

$$I_t = \left[\frac{i\eta\nu}{\nu+i\eta}\right]^a \Gamma(b+m)\Gamma(a+m)\Gamma(a) \times \frac{{}_2F_1(a,b,a+b+m,x)}{\Gamma(a+b+m)} , \tag{A1}$$

with a,b,m,x given by Eq. (17). A further use of the connection formula [Eq. 15.3.5) of Ref. 10] results in

$$I_t = \left[\frac{i\eta\nu}{\nu+i\eta}\right]^a \Gamma(a)\Gamma(a+m)\Gamma(b+m) \left[\frac{2\nu}{i\eta+\nu}\right]^{-b} g_a , \tag{A2}$$

where

$$g_a = \frac{{}_2F_1(b,b+m,a+b+m;y)}{\Gamma(a+b+m)}$$

and

$$y = \frac{\nu-i\eta}{2\nu} . \tag{A3}$$

Note that the series representation of g_a is convergent for $\eta < \sqrt{3}\nu$, and that by the recursion relation [Eq. (15.2.12) of Ref. 10]

$$(y-1)g_a+[a+b+m-(2a+m+1)y]g_{a+1}$$
$$+(a+m+1)(a+1)yg_{a+2}=0\ . \quad \text{(A4)}$$

Evaluating the sum

$$\sum_t b_t I_t = b_0 I_0 + b_1 I_1 + b_2 I_2 + \cdots \quad \text{(A5)}$$

of Eq. (14) can result in cancellation error because values of b_t and I_t are large and of varying sign. Instead the nesting procedure

$$b_0 I_0 \left[1 + \frac{b_1 I_1}{b_0 I_0} \left[1 + \frac{b_2 I_2}{b_1 I_1} (1 + \cdots \right) \right] \right] \quad \text{(A6)}$$

using only ratios which are smaller in value, and can be found easily from the recursion relation for the b_t [Eq. (5)] and for I_t [(A2)–(A4)].

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