Preconvolving theoretical photoabsorption cross sections using multichannel quantum-defect theory

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Formulas for the direct calculation of convolved photoabsorption cross sections are presented. Atomic parameters used for the calculation of infinite resolution cross sections can be used in a very accurate approximate formula for the convolved cross section. The direct calculation of convolved cross sections is usually 20–100 times faster than the calculation of numerically convolved cross sections. Numerically convolved cross sections are compared to the preconvolved cross section for a recent atomic calculation.

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I. INTRODUCTION

Multichannel quantum-defect theory (MQDT) uses information on the short-range properties of atoms and ions to obtain cross sections [1]. This is accomplished by utilizing functions that are solutions of the Schrödinger equation outside of the complicated region near the nucleus where the electrons can interact strongly. For example, in the photoionization of atoms the relevant information involves dipole matrix elements and the phase shifts and couplings between channels relative to a pure Coulomb potential; these parameters do not vary strongly with energy because the electrons are affected by very strong forces in the interaction region where the difference from a pure $1/r$ potential is strongest (i.e., small energy changes do not affect the dynamics in the interaction region). To calculate the cross section the long-range behavior of the Coulomb functions are utilized to obtain the cross section on a mesh much finer than that needed to describe the energy dependence of the short-range scattering parameters [1,2]. The cross section needs to be calculated on a fine mesh because the autoionizing Rydberg resonances can be quite narrow; as the threshold is approached the widths and spacings of the resonances decrease like $1/n^3$. To obtain a convolved calculated cross section which can be compared to experiment, the cross section needs to be calculated on a mesh approx. 100 times finer (at least) than the mesh for the experiment. A correct numerical convolution of a calculated cross section near a resonance needs approx. 10 points over the full width of the resonance which can be troublesome for sharp resonances; for example, in the lighter atoms very sharp resonances can result when a state is forbidden to decay in LS coupling but can decay through the weak spin-orbit interaction. This is a very wasteful procedure since all of the atomic dynamics is embodied in the short-range scattering parameters that do not vary much with energy. Therefore, it should be possible to obtain a convolved cross section *directly* from these smooth parameters without a numerical convolution.

The main advance described in this paper is the development of an approximate formula which uses MQDT parameters obtained at real energies for a direct calculation of the convolved cross section. The same parameters that appear in the calculation of an infinite-resolution photoabsorption cross section at energy E can be used to *directly* obtain the cross section at energy E that has been convolved over a width Γ. The approximate formula for the preconvolved cross section is accurate to the extent that the short-range MQDT parameters do not vary over the convolution width, Γ. This is usually an excellent approximation; in test calculations using atomic parameters from R-matrix calculations, the errors in the approximate preconvolved cross section were smaller than the errors in the numerically convolved cross section when the fine energy mesh was 50–1000 times smaller than Γ. The direct calculation of a convolved cross section is $\sim m_i/2m_c$ times faster than the numerical calculation of convolved cross sections where m_c is the number of mesh points for the convolved cross section and m_i is the number of fine energy mesh points of the infinite resolution cross section; m_i/m_c is usually larger than 50 and can be as large as 1000.

The developments discussed in this paper were spurred by the complexity of recent atomic calculations [3,4] and experiments. For these two systems (Sc [3] and Ba in a static electric field [4]), the R-matrix calculations of the MQDT parameters on a coarse energy mesh were very fast compared to the final calculations of the cross sections on a fine energy mesh. For example, the calculation [3] of the MQDT parameters for all relevant LS symmetries in Sc required $\sim$ 20 CPU minutes on a DEC5200 workstation; the calculation of the cross section on an energy mesh fine enough for a numerical convolution would have required over 100 CPU hours because of the large number of jj-coupled channels. Consequently, the experimental cross section was compared to the unconvolved

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theoretical cross section which was not completely satisfactory because a large number of features were not resolved in the experiment. In the future, atomic calculations will probably become even more complicated.

In this paper, the formulas for a direct calculation of convolved cross sections are presented. A simple single channel case is examined in detail to illustrate the nature of the convolved cross section near thresholds. Comparison with the photoabsorption cross section of Sc (in LS coupling) is presented graphically to illustrate the accuracy of the method for a recent atomic calculation; this comparison demonstrates the ability of the method to handle energy dependences in the short-range parameters.

II. WAVE FUNCTIONS AND DIPOLE MATRIX ELEMENTS

Before deriving the formulas needed to directly calculate the convolved cross section, it is useful to list those needed to obtain the infinite resolution cross section. Two of the standard forms for the wave function when the outer electron is outside of the interaction region are

$$\psi_k = A\sum_j \phi_j(f_j\delta_{jk} - g_j K_{jk}) \tag{1}$$

and

$$\psi_k^{(-)} = \tfrac{1}{2}A\sum_j \phi_j[(f_j + ig_j)\delta_{jk} + (f_j - ig_j)S^\dagger_{jk}], \tag{2}$$

where A is the antisymmetrization operator (which has no effect since the electron is outside of the interaction region), ϕ_j is the channel function incorporating all of the degrees of freedom except the radial motion of the outer electron, and f_j and g_j are Coulomb functions at energy $E - E_j$ (E_j is the energy of the core electrons in state ϕ_j) and orbital angular momentum ℓ_j. The form of the wave function is much more complicated when all of the electrons are in the interaction region. The only other parameters, besides $\underline{S}^\dagger$ or $\underline{K}$, needed to obtain the cross section are the dipole matrix elements connecting these wave functions to the ground state:

$$D_k = \langle\Psi_g|D|\psi_k\rangle, \tag{3}$$

$$D_k^{(-)} = \langle\Psi_g|D|\psi_k^{(-)}\rangle, \tag{4}$$

where the integrals are over the full volume. $D^{(-)}$ and $\underline{S}^\dagger$ can be obtained from D and $\underline{K}$ giving

$$\underline{S}^\dagger = (\underline{1} - i\underline{K})/(\underline{1} + i\underline{K}), \tag{5}$$

$$D_k^{(-)} = \sum_j D_j(\underline{1} + i\underline{K})^{-1}_{jk}. \tag{6}$$

(Note: The definition of $\psi_k^{(-)}$ differs from more usual definitions [5]; the phase shift from the Coulomb field has not been incorporated because it does not have any effect on the total cross section.)

The form of these functions apply even when some of the channels are closed; i.e., $E - E_j < 0$. However, in this case these functions are not physical because they diverge in the closed channels. To obtain the physical wave functions, the unphysical functions are superposed to eliminate the exponentially diverging part of the wave function in all of the closed channels. To choose the correct superposition it is only necessary to know that at positive real energies the f_j and g_j are normalized per unit energy and at negative real energies they both diverge but their ratio goes to a constant, $f_j/g_j \to -\tan\pi\nu_j$, as $r \to \infty$ where $\nu_j = 1/\sqrt{2(E_j - E)}$. The correct superposition is

$$\psi_o^{(-)\text{phys}} = \psi_o^{(-)} - \psi_c^{(-)}(S^\dagger_{cc} - e^{2i\pi\nu})^{-1}S^\dagger_{co}, \tag{7}$$

which gives for the physical dipole matrix element

$$D_o^{(-)\text{phys}} = D_o^{(-)} - D_c^{(-)}(S^\dagger_{cc} - e^{2i\pi\nu})^{-1}S^\dagger_{co}, \tag{8}$$

where the subscripts o and c refer to the open and closed subspaces; for example, the matrix $S^\dagger_{cc} - \exp(2i\pi\nu)$ is a matrix of dimension $n_c \times n_c$ (n_c is the number of closed channels) whose elements are $S^\dagger_{jk} - \delta_{jk}\exp(2i\pi\nu_j)$ where both channels j and k are closed.

The description of the atomic dynamics in terms of the short-range parameters is advantageous because it naturally incorporates the interaction of channels; for most purposes it is not natural to incorporate the interaction on a state-by-state basis. Because the $D^{(-)}$ and $\underline{S}^\dagger$ do not depend strongly on energy, the dynamics of Rydberg and continuum states can be related to each other. If there are open channels, $\underline{S}^\dagger_{cc}$ is not a unitary matrix; the positions and widths of resonances can be obtained from $\underline{S}^\dagger_{cc}$ and the positions of the thresholds. The decay rates of the resonances into the open channels can be obtained from $\underline{S}^\dagger_{cc}$ and $\underline{S}^\dagger_{co}$. Because the short-range parameters do not depend strongly on energy, interactions describable by a frame transformation [6] can be easily incorporated.

There are two important properties of this treatment that should be noted. The first is that the open and the closed channels are treated differently. The second is that the $D_o^{(-)\text{phys}}$ and the cross section oscillate extremely fast just below threshold. As a threshold is crossed, $D_o^{(-)\text{phys}}$ changes discontinuously from n_o open channels to a smooth cross section with $n_o + m$ open channels (m is the number of Rydberg series attached to the threshold). This sort of behavior is not seen in experiments; in the experiments, the widths of the states gets smaller than the resolution as the threshold is approached after which the heights of the resonances decrease like $1/n^3$ until they smoothly merge onto the above threshold cross section. Convolved physical quantities just below threshold were explored by Gailitis [7]. Because the widths of the resonances decrease like $1/n^3$ (but the heights remain constant) and the spacing of the resonances decrease like $1/n^3$, the experimental resolution near threshold will always be broader than the spacing; therefore, there will always be a region just below threshold where the density of resonances is high enough that it appears to be a

continuum in the experiment.

The method described below automatically reproduces the effects of finite resolution on the cross section near threshold. The behavior of the cross section near an extremely sharp, isolated resonance which is smeared by finite resolution also emerges naturally. However, the method is still based on the short-range parameters and therfore retains the power of the usual MQDT formulation.

III. COULOMB FUNCTIONS AT COMPLEX ENERGIES

The method for preconvolving photoabsorption cross sections, described in the next section, involves a MQDT-like formulation for the inhomogeneous function at complex energies. The strength of MQDT formulations is that the asymptotic form of the wave function is determined analytically in terms of parameters that can be obtained at relatively short distances; these parameters usually do not have a strong dependence on energy. In Eqs. (27) and (30) the inhomogeneous function is determined at energies with a positive imaginary component. The asymptotic form of the Coulomb functions as defined in this paper will only be given for the upper half of the complex energy plane.

Once the form of the two linearly independent Coulomb functions is defined near the origin ($r \sim 0$) the asymptotic forms as $r \to \infty$ can be obtained from standard works [1,2]; to simplify the references the formulas presented here will be connected with those of Seaton [1]. The regular (f) and irregular (g) Coulomb functions are chosen so they are identical on the real energy axis to the f and g used for photoionization calculations [2]. These functions are defined to be

$$f_{E_r+iE_i,\ell} = \sqrt{B(E_r+iE_i,\ell)}\,y(\kappa,\ell+\tfrac{1}{2},z), \tag{9}$$

$$g_{E_r+iE_i,\ell} = [\eta(\kappa,\ell+\tfrac{1}{2},z) - i\mathrm{Im}[G(\kappa,\ell)]y(\kappa,\ell+\tfrac{1}{2},z)]/\sqrt{B(E_r+iE_i,\ell)}, \tag{10}$$

where $\mathrm{Im}[z]$ is the imaginary part of z and E_r and E_i are real with $E_i > 0$ and

$$\varepsilon e^{i\phi} = E_r + iE_i, \quad 0 < \phi < \pi,\ \varepsilon > 0, \tag{11}$$

$$\kappa = e^{-i(\phi-\pi)/2}/\sqrt{2\varepsilon}, \tag{12}$$

$$z = 2r/\kappa. \tag{13}$$

The functions y and η are related to the Whittaker functions by

$$y(\kappa,\lambda,z) = \kappa^{\lambda+1/2}e^{i\pi\kappa}[e^{-i\pi(\lambda+1/2)}W_{\kappa,\lambda}(z)/\Gamma(\kappa+\lambda+\tfrac{1}{2}) + W_{-\kappa,\lambda}(e^{i\pi}z)/\Gamma(-\kappa+\lambda+\tfrac{1}{2})], \tag{14}$$

$$\eta(\kappa,\lambda,z) = \cot[\pi(\lambda+\tfrac{1}{2}-\kappa)]A(E_r+iE_i,\ell)y(\kappa,\lambda,z) - \Gamma(\lambda+\tfrac{1}{2}-\kappa)W_{\kappa,\lambda}(z)/(\pi\kappa^{\lambda-1/2}). \tag{15}$$

Finally, the constants A, G, and B are defined by

$$A(E_r+iE_i,\ell) = \Pi_{p=0}^{p=\ell}[1+2p^2(E_r+iE_i)], \tag{16}$$

$$G(\kappa,\ell) = \frac{A(E_r+iE_i,\ell)}{2\pi}[\psi(\kappa+\ell+1) + \psi(\kappa-\ell) - 2\ln(\kappa)], \tag{17}$$

$$B(E_r+iE_i,\ell) = A(E_r+iE_i,\ell) + \mathrm{Im}[G(\kappa,\ell)], \tag{18}$$

and $\psi(x) = d\ln\Gamma(x)/dx$. These definitions ensure that as $E_i \to 0+$ the functions f and g go over to their real energy values as defined in previous works. These definitions only hold when the imaginary part of the energy is positive but it is relatively straightforward to find similar functions when the imaginary part of the energy is negative.

To find the asymptotic form of f and g it is necessary to know the asymptotic form of the Whittaker function

$$W_{\kappa,\lambda}(z) \to z^{\kappa}e^{-z/2}, \quad z \to \infty. \tag{19}$$

In MQDT the asymptotic form of the wave function (and the inhomogeneous function for this paper) is used to analytically construct the physical function (functions that converge to zero in the closed channels instead of diverging and have the correct oscillatory property in the open channels). The f and g functions diverge as $r \to \infty$ at all energies with a nonzero imaginary term. To find the correct superposition of f and g that converges to zero as $r \to \infty$ it is only necessary to know the ratio f/g as $r \to \infty$ or equivalently the ratio $(f+ig)/(f-ig)$. With the definition of f and g given above this ratio is

$$(f+ig)/(f-ig) = -e^{2i\pi\kappa}(1+\alpha)+\alpha, \quad r \to \infty, \tag{20}$$

where $\alpha = \mathrm{Im}[G]/A$. At large positive energies $\kappa \to i/\sqrt{2\varepsilon}$ and $\alpha \to 1/[\exp(-2i\pi\kappa)-1]$ which means the ratio $(f+ig)/(f-ig) \to 0$ at large positive energies as $r \to \infty$. Since the factor α is moderately difficult to evaluate compared to the exponential factor, an approximate form for the ratio is used. This approximate form is

$$(f_j+ig_j)/(f_j-ig_j) \simeq -e^{2i\beta_j}, \tag{21}$$

with

$$\beta_j = \pi\kappa_j, \quad E_r - E_j < 0, \tag{22}$$

$$\beta_j = i\infty, \quad E_r - E_j > 0. \tag{23}$$

The error in this approximate ratio is proportional to E_i and goes very rapidly to zero for $E_r - E_j > 0$. Note that the discontinuity in β_j has no practical effect since the size of the discontinuity in the ratio $(f_j + ig_j)/(f_j - ig_j)$ is equal to $\exp(-\pi/\sqrt{E_i})$; for $E_i = 0.01$ a.u. $\simeq 1/4$ eV the discontinuity in the ratio is $\sim 10^{-14}$ and for $E_i = 10^{-3}$ a.u. the discontinuity in the ratio is $\sim 10^{-43}$. Typically E_i is much less than 10^{-3} a.u. in photoabsorption experiments. For all practical purposes, the ratio Eq. (21) can be considered a continuous function of energy.

IV. CONVOLVED CROSS SECTIONS

The procedure that is presented here is based on applying ideas for the calculation of the frequency-dependent polarizability of an atom [8,9]. The cross section in the length gauge is

$$\sigma(\omega) = C\omega \sum_j \langle \Psi_g | D | \psi^{(-)\text{phys}}_{E_g+\omega,j} \rangle \langle \psi^{(-)\text{phys}}_{E_g+\omega,j} | D | \Psi_g \rangle, \tag{24}$$

where Ψ_g is the ground state wave function, $\psi^{(-)\text{phys}}_{E_g+\omega,j}$ is the jth independent (physical) wave function at energy $E_g + \omega$ which has outgoing waves only in channel j, ω is the frequency of the light, and C is a constant that depends on whether the calculation is being performed in LS coupling, jj coupling, etc. The cross section can be convolved with a weight function that mimics an experimental resolution Γ (full width at half maximum). This convolved cross section is

$$\sigma^{(2)}(\omega_0) = \frac{1}{2\pi} \int d\omega \sigma(\omega) \Gamma / [(\omega - \omega_0)^2 + (\Gamma/2)^2] \tag{25}$$

with the superscript (2) denoting a Lorentzian convolution. By substituting the expression for the cross section, Eq. (24), into Eq. (25) and setting $\omega \equiv E - E_g$, the convolved cross section can be expressed as

$$\sigma^{(2)}(\omega_0) = -\frac{C}{\pi} \text{Im} \left[\left(\omega_0 + \frac{i\Gamma}{2} \right) \sum_j \int dE \langle \Psi_g | D | \psi^{(-)\text{phys}}_{Ej} \rangle \langle \psi^{(-)\text{phys}}_{Ej} | D | \Psi_g \rangle \left(E_g + \omega_0 + \frac{i\Gamma}{2} - E \right)^{-1} \right], \tag{26}$$

where $\text{Im}[z]$ is the imaginary part of z. The important point is that the summation and integration can be formally carried out so that the convolved cross section can be written in the form

$$\sigma^{(2)}(\omega_0) = -\frac{C}{\pi} \text{Im} \left[(\omega_0 + i\Gamma/2) \left\langle \Psi_g | D | \Lambda \left(E_g + \omega_0 + \frac{i\Gamma}{2} \right) \right\rangle \right], \tag{27}$$

where

$$(E - H)\Lambda(E) = D\Psi_g \tag{28}$$

with $E = E_g + \omega_0 + i\Gamma/2 = E_r + i\Gamma/2$.

Actually, a Lorentzian convolution is a poor approximation to an experimental spectrum with resolution Γ because of the long tail. A better form to use for the convolved cross section is

$$\sigma^{(4)}(\omega_0) = \frac{\sqrt{2}}{\pi} \int d\omega \sigma(\omega) (\Gamma/2)^3 / [(\omega - \omega_0)^4 + (\Gamma/2)^4]. \tag{29}$$

It can be shown that this convolved cross section is equal to

$$\sigma^{(4)}(\omega_0) = -\frac{C}{\sqrt{2}\pi} \text{Im} \left[\frac{1}{\sqrt{i}} \{ (\omega_0 + \sqrt{i}\Gamma/2) \langle \Psi_g | D | \Lambda(E_g + \omega_0 + \Gamma/2\sqrt{2} + i\Gamma/2\sqrt{2}) \rangle \right.$$

$$\left. - (\omega_0 - \sqrt{i}\Gamma/2) \langle \Psi_g | D | \Lambda(E_g + \omega_0 - \Gamma/2\sqrt{2} + i\Gamma/2\sqrt{2} \rangle^* \} \right], \tag{30}$$

where $\sqrt{i} = (1 + i)/\sqrt{2}$. The form of the convolution function was chosen because the simple form of Eq. (30) results.

Equation (28) could be solved at slightly complex energies using the method of Refs. [8,9]. Although this is fairly easy to do and only involves slight modification of existing computer programs, the discussion in the next section shows that the dipole matrix elements needed for $\sigma^{(2)}(\omega_0)$ and $\sigma^{(4)}(\omega_0)$ can be obtained without actually solving Eq. (28). This development allows the calculation of preconvolved cross sections from the same parameters used for the calculation of infinite resolution cross sections.

V. APPROXIMATE DIPOLE MATRIX ELEMENTS

In this section, an approximate form for the dipole matrix elements in the convolved cross sections, $\sigma^{(2)}(\omega_0)$ and $\sigma^{(4)}(\omega_0)$, are given in terms of atomic parameters obtained at real energies; it is not necessary to solve Eq. (28) in this approximation. This is the most important advance presented in this paper since it allows the direct calculation of convolved cross sections from parameters that are already available; with this approximation the infinite resolution cross section and the preconvolved cross section can be obtained from the same parameters.

The approximation discussed in this section depends on the slow variation of the MQDT parameters (i.e., as long as the MQDT parameters do not vary over the convolution width, Γ, the results are accurate). This is a very good approximation for most systems.

The inhomogeneous function, $\Lambda(E)$, is completely determined by Eq. (28) and the fact that it must converge to zero as r (the electronic distance from the nucleus) goes to infinity at complex energies. However, because $\Lambda(E)$ is the physical solution, it incorporates the boundary conditions as $r \to \infty$ which can give it a very rapid dependence on energy. It is crucial that the fast energy dependence be expressed in closed form so that it is not necessary to recalculate the atomic dynamics on a fine energy mesh. With this in mind we use the smooth inhomogeneous function of Ref. [9] and the solutions, Eq. (2), of Schrödinger's equation to re-express the physical inhomogeneous function as

$$\Lambda(E) = \Lambda_s(E) + \sum_i \psi_{Ei}^{(-)} A_i(E), \tag{31}$$

where $\Lambda_s(E)$ is a solution of the inhomogeneous equation (28) with the asymptotic form

$$\Lambda_s(E) = A \sum_j \phi_j (f_j + i g_j) \lambda_j(E) \tag{32}$$

for all channels, j, whether open or closed. Because the asymptotic form of Λ_s does not depend on whether a particular channel is open or closed, it should not depend strongly on energy. In Eq. (31) neither Λ_s nor $\psi_j^{(-)}$ depend strongly on energy; the fast energy dependences are contained in the coefficients, A_j, of the smooth wave functions, $\psi_j^{(-)}$. The $\lambda_j(E)$ can be directly obtained from Eqs. (28) and (32) by using the solutions, Eq. (1), of the Schrödinger's equation and integration by parts:

$$\int dV \psi_j (E - H) \Lambda_s(E) = \int dV \psi_j D \Psi_g = D_j. \tag{33}$$

The D_j are real at real energies. The left hand side can be rewritten as

$$\int dV \left\{ [(E - H)\psi_j]\Lambda_s(E) + \frac{1}{2}\frac{\partial}{\partial r}\left[\psi_j \frac{\partial \Lambda_s(E)}{\partial r} - \frac{\partial \psi_j}{\partial r}\Lambda_s(E)\right]\right\}. \tag{34}$$

However, $(E-H)\psi_{Ej} = 0$ and the Wronskian in brackets can be evaluated from the asymptotic form of Λ_s and ψ_j which gives

$$\int dV \psi_j (E - H) \Lambda_s(E) = \sum_k \lambda_k(E)(i\delta_{kj} + K_{kj})/\pi. \tag{35}$$

Combining Eq. (33) with (35) gives a matrix equation for $\lambda_k(E)$ which can be inverted to yield

$$\lambda_j(E) = \pi \sum_k D_k (i + K)^{-1}_{kj} = -i\pi D_j^{(-)*}(E), \tag{36}$$

where Eq. (6) was used for the last step. This shows that the asymptotic form of $\Lambda_s(E)$ can be found without solving the inhomogeneous Eq. (28). The $D_j^{(-)}$ do not vary strongly with energy and therefore (as expected) the λ_j do not depend strongly on energy; it is a good approximation to use the value $D_j^{(-)}(E_r)$ for $D_j^{(-)}(E_r + iE_i)$ as long as $D_j^{(-)}(E)$ does not vary much over an energy range comparable to E_i.

The values of $A_j(E)$ can be quickly determined because the asymptotic form of $\Lambda_s(E)$ and $\psi_{Ej}^{(-)}$ are known. Asymptotically $\Lambda(E)$ must go to zero as $r \to \infty$ at complex energies in every channel, k. This condition determines the $A_j(E)$ completely from the equation

$$-2e^{2i\beta_k}\lambda_k + \sum_j (S^\dagger_{kj} - e^{2i\beta_k}\delta_{kj}) A_j = 0. \tag{37}$$

This equation is obtained by setting the coefficients of the exponentially diverging terms in Eq. (31) to zero. Substituting the value for λ_k and inverting this matrix equation yields the form of A_k:

$$A_k(E) = -2\pi i \sum_j (S^\dagger - e^{2i\beta})^{-1}_{kj} e^{2i\beta_j} D_j^{(-)*}. \tag{38}$$

$\mathbf{S}^\dagger$ is unitary but the matrix $\exp(2i\beta)$ is not unitary at complex energies; therefore, A_k can never truly diverge but has a very fast energy dependence when $\det[\mathbf{S}^\dagger - \exp(2i\beta)] \sim 0$. Note: $A_k = 0$ if $E_r - E_j > 0$ for all j [see Eq. (23)].

From these equations and physical reasoning we can give a closed form for the matrix element of Eqs. (27) and (30). This form is

$$\langle \Psi_g | D | \Lambda(E) \rangle = \langle \Psi_g | D | \Lambda_s(E) \rangle + \sum_k \langle \Psi_g | D | \psi_{Ek}^{(-)} \rangle A_k(E) \tag{39}$$

$$= \langle \Psi_g | D | \Lambda_s(E) \rangle - 2\pi i \sum_{k,j} D_k^{(-)} (S^\dagger - e^{2i\beta})^{-1}_{kj} e^{2i\beta_j} D_j^{(-)*}, \tag{40}$$

where we have used the expressions in Eqs. (31) and (38). Note that all of the factors in Eq. (40) are obtained from atomic calculation except for the dipole matrix element between the ground state and the smooth inhomogeneous function. To completely obtain the matrix element $\langle \Psi_g | D | \Lambda_s \rangle$ it is necessary to solve the inhomogeneous equation (28) with the boundary conditions of Eq. (32). However, the imaginary part of this term can

be obtained from physical reasoning. If all channels are open ($E_r - E_j > 0$ for all j), then $\exp(2i\beta_j) = 0$ for all of the channels which gives

$$\langle \Psi_g|D|\Lambda(E)\rangle = \langle \Psi_g|D|\Lambda_s(E)\rangle. \tag{41}$$

The cross section will then be

$$\sigma^{(2)}(\omega_0) = -\frac{C}{\pi}\mathrm{Im}[(\omega_0 + i\Gamma/2)\langle \Psi_g|D|\Lambda_s(E)\rangle], \tag{42}$$

where $\mathrm{Im}[z]$ is the imaginary part of z. When $\Gamma = 0^+$

$$\sigma^{(2)}(\omega_0) = C\omega_0 \sum_k D_k^{(-)}(E_r)D_k^{(-)*}(E_r)$$
$$= -\frac{C}{\pi}\omega_0 \mathrm{Im}[\langle \Psi_g|D|\Lambda_s(E_r)\rangle]. \tag{43}$$

Since the Λ_s does not depend strongly on energy, the approximation

$$\langle \Psi_g|D|\Lambda_s(E_r + iE_i)\rangle \simeq -i\pi \sum_k D_k^{(-)}(E_r)D_k^{(-)*}(E_r) \tag{44}$$

gives the imaginary part very well; using $D_k^{(-)}(E_r)$ for $D_k^{(-)}(E_r + iE_i)$ is a very good approximation because the $D^{(-)}$ typically vary on energy scales of 0.1 a.u. which should be compared to typical values of E_i (10^{-6} a.u.$< E_i < 10^{-3}$ a.u.). The real part of $\langle \Psi_g|D|\Lambda_s\rangle$ can be of the same size as the imaginary part. However, the real part does not contribute much to the cross section since it is multiplied by Γ in Eq. (27) and in Eq. (30) it only contributes proportional to

$$(\langle \Psi_g|D|\Lambda_s(E + \Gamma/2\sqrt{2})\rangle - \langle \Psi_g|D|\Lambda_s(E - \Gamma/2\sqrt{2})\rangle)\omega_0, \tag{45}$$

which is very small since $\langle \Psi_g|D|\Lambda_s\rangle$ does not vary rapidly with energy.

The final form for the physical matrix element connecting the ground state and the inhomogeneous function is

$$\langle \Psi_g|D|\Lambda(E_r + iE_i)\rangle \simeq -i\pi \sum_k D_k^{(-)}\left[D_k^{(-)*} + 2\sum_j (S^\dagger - e^{2i\beta})^{-1}_{kj} e^{2i\beta_j} D_j^{(-)*}\right], \tag{46}$$

where the $D_k^{(-)}$ and $S^\dagger_{kj}$ are evaluated at energy E_r and $\beta_j = \pi/\sqrt{2(E_j - E_r - iE_i)}$ when $E_r - E_j < 0$ and $\beta_j = i\infty$ when $E_r - E_j > 0$. The energy of the core is E_j and the branch of the square root is chosen so the imaginary part of β_j is positive. The importance of this formula derives from the fact that every term is obtained from atomic calculations so there is no need to solve Eq. (28) for the inhomogeneous function. If the exact asymptotic forms of f and g are used, the $\exp(2i\beta_j)$ in Eq. (46) should be replaced by $\exp(2i\pi\kappa_j)(1 + \alpha_j) - \alpha_j$ [see Eqs. (20) and (23) and the discussion of that paragraph]. The approximations needed to obtain Eq. (46) no longer apply when $\mathbf{S}^\dagger$ and $D^{(-)}$ vary substantially over an energy range comparable to E_i. Equation (46) can be written in a more symmetrical form.

The dipole matrix element, Eq. (46), that goes into the cross section clearly displays a point of physics that is not obvious from the formula for the infinite resolution cross section, Eqs. (7) and (24). For the infinite resolution cross section, one must keep track of the open and closed channels because they are treated differently. As a threshold is approached, the cross section oscillates faster and faster until just below the threshold it is oscillating infinitely fast; just above threshold the channel is treated as open and the cross section is smooth. In Eq. (46), there is no distinction between the open and the closed channels. The $\exp(2i\beta_j)$ "closes" the channel or "opens" it automatically. Far below threshold (compared to E_i) the magnitude of $\exp(2i\beta_j)$ is nearly one and it oscillates as in the usual MQDT formulas. However, as the threshold is approached, the magnitude of this factor rapidly decreases until just above threshold where the magnitude is zero and remains zero at higher energies. This gives the correct behavior to the cross section; the Rydberg series decrease in height like $1/n^3$ once the natural widths of the lines become smaller than the convolution width Γ until they become completely washed out; the convolved cross section goes smoothly through the threshold.

The partial cross sections cannot be averaged in the same way as the total cross section since the prescription in this paper is for averaging *photoabsorption* cross sections; the partial cross section involves the dynamics of the atom after the photon has been absorbed. A more detailed understanding of the roles of the coefficients of the incoming and outgoing wave terms in the inhomogeneous function is necessary before preconvolved partial cross sections can be obtained.

VI. RESULTS

A. Single channel cross section

It is instructive to investigate the behavior of the preconvolved photoabsorption cross section for a one-channel problem. For this case the cross section can be obtained in closed form:

$$\sigma^{(2)}(\omega_0) = C|D^{(-)}|^2 \mathrm{Re}\{(\omega_0 + i\Gamma/2)[1 + 2e^{2i\beta}/(e^{-2i\pi\mu} - e^{2i\beta})]\}, \tag{47}$$

where $\exp(-2i\pi\mu) = S^{\dagger}$ and Re[z] is the real part of z. At an energy far below threshold compared to Γ [i.e., where the Rydberg spacing is $(n-\mu)^{-3} >> \Gamma$], the magnitude of $\exp(2i\beta)$ is nearly equal to one. Expanding β near a resonance energy $E_n = -1/2(n-\mu)^2$ (the core energy is defined to be zero) gives

$$\beta \simeq \pi[n - \mu + (n-\mu)^3(\omega_0 + i\Gamma/2 - \omega_n)], \quad (48)$$

where $\omega_n = E_n - E_g$ is the frequency of the resonance above the ground state. Substituting this expression into Eq. (47) gives the approximate expression

$$\sigma^{(2)}(\omega_0) \simeq C|D^{(-)}|^2\omega_n \frac{\Gamma}{2\pi(n-\mu)^3}[(\omega_0-\omega_n)^2 + (\Gamma/2)^2]^{-1}, \quad (49)$$

which clearly shows the photoabsorption cross section to consist of Lorentzian peaks whose heights decrease like $(n-\mu)^{-3}$; the peaks are Lorentzian because the convolution function was taken to be Lorentzian, Eq. (25).

As the threshold is approached the Im[β] increases until just above threshold $\exp(2i\beta) = 0$. Within a few Γ of threshold and above threshold, the preconvolved cross section can be approximated by

$$\sigma^{(2)}(\omega_0) \simeq C|D^{(-)}|^2\omega_0(1 + 2\mathrm{Re}[e^{2i(\pi\mu+\beta)}]) \quad (50)$$

$$= C|D^{(-)}|^2\omega_0[1 + 2e^{-2\beta_i}\cos(2\pi\mu + 2\beta_r)], \quad (51)$$

where $\beta_r = \mathrm{Re}[\beta]$ and $\beta_i = \mathrm{Im}[\beta]$. This formula is very satisfying because it shows how the convolved photoabsorption cross section evolves smoothly from below threshold to the continuum value above threshold. This smooth evolution also holds for autoionizing resonances as shown in the figures of the next section.

B. Graphical comparison with numerically convolved cross section

In Figs. 1 and 3 the unconvolved cross section for $(4s3d)\ ^1D5s\ ^2D \rightarrow\ ^2F^o$ photoabsorption by Sc is shown.

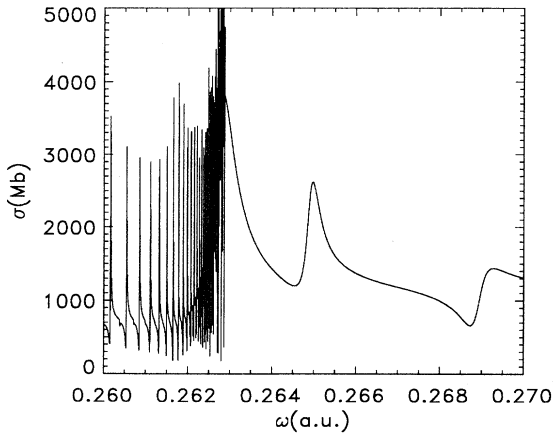

FIG. 1. The photoabsorption cross section from an excited state of Sc calculated on a fine energy mesh of 10^{-6} a.u.

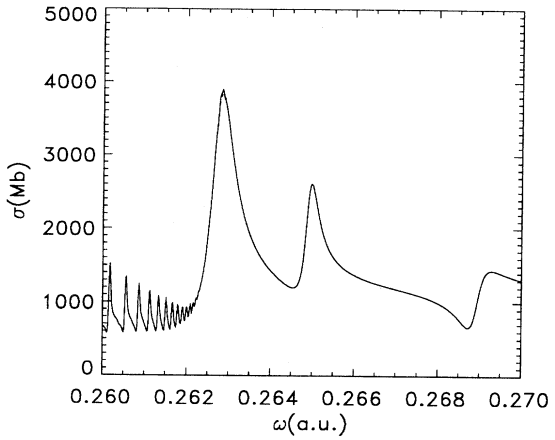

FIG. 2. The numerically convolved and preconvolved cross sections with $\Gamma = 5 \times 10^{-5}$. Differences between the two curves can hardly be seen; any differences are due to errors in the numerically convolved cross section.

This cross section was obtained from an R-matrix calculation [10] and therefore all of the short-range parameters, $\mathbf{S}^{\dagger}$ and $D^{(-)}$, have realistic energy dependences. These figures have the typical signature of unconvolved cross sections (especially note the blackened area just below the various thresholds where the cross section oscillates faster than the thickness of a line). In Figs. 2 and 4, the cross section is shown convolved numerically and from Eqs. (30) and (46) with $\Gamma = 5 \times 10^{-5}$ a.u.; the differences between the two curves cannot be seen on these figures. The fine energy spacing of the unconvolved cross section was 10^{-6} a.u. Plotting the difference in the two convolved cross sections only shows the errors in the numerically convolved cross section; i.e., although the energy spacing of the unconvolved cross section was $\Gamma/50$, the numerically convolved cross section was less accurate than the approximate preconvolved cross section. The effect of the convolution is easier to see in Figs. 1 and 2 because the spectrum is simpler in that region; especially notice the smooth tapering of the convolved Rydberg series to its continuum value just above threshold. Figures

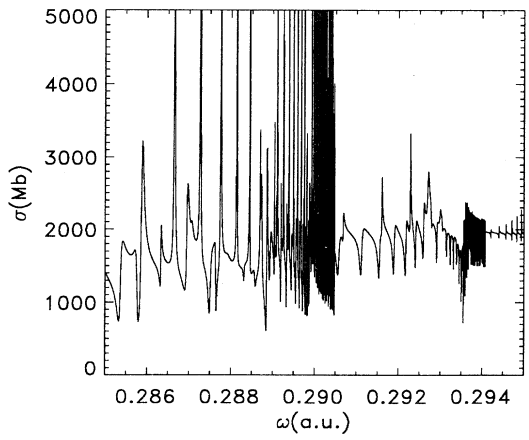

FIG. 3. Same as Fig. 1.

3 and 4 show a more complicated region of the spectrum and illustrate how the method described in this paper can preconvolve spectra involving many interacting Rydberg series. The calculation of the preconvolved spectrum was more than 20 times faster than the calculation of the numerically convolved spectrum.

VII. CONCLUSIONS

The formulas for the *direct* calculation of convolved photoabsorption cross section have been derived in terms of the parameters used for (infinite resolution) theoretical cross section. In this formulation it is not necessary to waste effort calculating the cross section on an extremely fine mesh before numerically convolving and therefore allows direct calculation of cross sections which can be compared to experiment. The direct calculation of convolved cross sections is more than an order of magnitude faster than the numerical convolution. These formulas do not distinguish between open and closed channels and can explain the smooth evolution of experimental or convolved theoretical cross sections through thresholds in a natural way. This formulation provides a nice practical and conceptual tool for the theoretical study of spectra.

An approximate formula for the matrix elements was obtained in terms of atomic parameters calculated at real energies; this approximate formula works well as long as the MQDT parameters do not vary over energy ranges comparable to the convolution width. This is usually an excellent approximation. The formulas derived in this paper only apply for photoabsorption by neutral species.

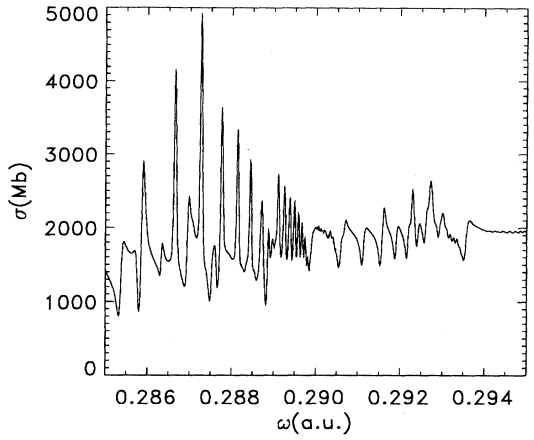

FIG. 4. Same as Fig. 2.

The application of the ideas in this paper to photoabsorption by atoms in external fields or by ions should be straightforward.

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