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Algebraic variational approach to atomic and molecular photoionization cross sections: Removing the energy dependence from the basis

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We describe a variational method for calculating photoionization cross sections from a matrix element of the resolvent operator. Scattering boundary conditions are enforced by expanding the resolvent in a basis of square-integrable (L^2) and outgoing wave continuum basis functions. By employing several continuum basis functions, with overlaps defined by a suitable analytic continuation, we can, in a single calculation, express the cross section over a continuous range of energies without explicitly resolving the variational equations at each desired energy. The method is illustrated by calculation of the photoionization cross section of atomic Be in the autoionizing region between the $1s^2 2s$ and $1s^2 2p$ states of Be$^+$. [S1050-2947(97)02301-9]

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I. INTRODUCTION

Advances in theory, combined with the power provided by today's high-end computers, have contributed significantly to our ability to accurately evaluate photoionization cross sections from first principles. In the case of atomic targets, numerous methods are available for obtaining accurate electron-ion continuum wave functions by direct numerical integration of the Schrödinger equation and a variety of techniques, such as the multiconfiguration Hartree-Fock method [1], are available for incorporating correlation effects into the calculated cross sections. Nevertheless, there are many cases in which difficulties associated with direct numerical computation of electron-ion scattering wave functions by numerical integration of the close-coupling equations makes analytic expansion methods a practical alternative for the *ab initio* calculation of photoionization cross sections, particularly for molecular targets. Several approaches have been developed. One category includes a variety of ''L^2 methods,'' which attempt to avoid the explicit imposition of scattering boundary conditions and employ only square-integrable basis functions. The most widely applied methods of this type are the Stieltjes moment theory approach [2] and the rotated coordinate or complex basis function method [3]. On the other hand, there are a number of variational methods that have been extensively developed and applied over the past decade to electron-molecule collision problems. These include the R-matrix method [4], the multichannel Schwinger method [5], and the complex Kohn variational method [6]. In these methods, scattering boundary conditions are enforced either through a matching procedure (R matrix), through the use of variational expressions based on the Lippman-Schwinger equation (Schwinger method), or through the use of continuum functions in the trial function (complex Kohn).

The problem we wish to address here is the comparative ability of these methods to treat the energy dependence of the photoionization cross section in regions dominated by autoionization peaks. Stieltjes imaging is notoriously difficult to apply in such cases. The Stieltjes moment method essentially averages the energy dependence of the cross section over an underlying, discrete pseudospectrum. In practical applications, it is difficult to make this spectrum dense enough to resolve very sharp energy features, effectively limiting the method to cases where the cross section varies smoothly with energy. The method can be modified via the use of projection operators to study the case of isolated resonances [7], but the technique is ill suited to energy regions dominated by many autoionizing states. The same is true of the method of complex basis functions. While the latter is quite useful in direct calculations of resonance energies and lifetimes [8], these parameters generally depend rather sensitively on the basis and a careful optimization of the nonlinear parameters (rotation angle) is generally required to achieve accurate results. In photoionization applications, it may be difficult to tune a single basis to provide both an accurate representation of the background continuum as well as a series of sharp resonances [9].

Of the variational methods, the R matrix [4] is particularly well suited to the kind of problem we have in mind, since it provides a method for rapid evaluation of the cross section at any energy once all the R-matrix eigenvalues have been determined. In the standard Schwinger and Kohn methods, the variational equations must be resolved at each energy. This may be computationally intensive in situations where many points are needed to resolve a highly structured cross section. In this paper we describe a modification of the complex Kohn approach that shares the desirable feature of R-matrix theory of allowing for rapid calculation of the cross section at any energy after a single diagonalization of the Hamiltonian. Unlike R-matrix theory, however, the method does not require basis functions to be normalized over a sphere of finite volume, which complicates the evaluation of Hamiltonian matrix elements, particularly for polyatomic targets. In the next section, we describe our theoretical approach for computing the total photoionization cross section. In Sec. III we present some results for the case of atomic Be. Section IV contains some concluding remarks and a discussion of the modifications necessary to obtain partial cross sections and angular distributions.

II. METHOD

In first-order perturbation theory, the total photoabsorption cross section is related to the negative frequency component of the dipole polarizability

$$\alpha^{-}(\omega)=\lim_{\varepsilon\to 0}\left\langle \Psi_0\left|\mu\,\frac{1}{H-E_0-\omega-i\varepsilon}\,\mu\right|\Psi_0\right\rangle \tag{1}$$

through the relation [10]

$$\sigma(\omega)=(4\pi\omega/c)\mathrm{Im}[\alpha^{-}(\omega)], \tag{2}$$

where H is the Hamiltonian of the target in initial state Ψ_0 with energy E_0, ω is the photon energy, and μ is the dipole operator. Equation (2) is easily verified by inserting a spectral expansion of H into Eq. (1) and evaluating the residue at $z=\omega+i\varepsilon$. Many basis set techniques proceed by approximating the resolvent

$$G^{+}(E)=\lim_{\varepsilon\to 0}\frac{1}{H-E-i\varepsilon} \tag{3}$$

in the generic form

$$G^{+}(E)\approx\sum_{i,j}\;|\phi_i\rangle(\langle\phi_i|H-E|\phi_j\rangle)^{-1}\langle\phi_j|, \tag{4}$$

where $\{\phi_i\}$ is some set of basis functions and $(\langle\phi_i|H-E|\phi_j\rangle)^{-1}$ is the ijth element of the inverse of the matrix $\langle\phi_i|H-E|\phi_j\rangle$. The basic attraction of these methods is that scattering calculations are reduced to matrix element evaluation and linear algebra. Of course, the simplest approximation—choosing $\{\phi_i\}$ to be a set of real, square-integrable functions—does not work for real energies, because it fails to incorporate the proper outgoing wave boundary conditions, producing instead an approximation to $G^{+}(E)$ marked by a series of poles at the real eigenvalues of $\langle\phi_i|H|\phi_j\rangle$. To address this problem, several methods have been proposed, including the use of analytic continuation [11] and complex-scaled basis functions [3]. We focus here on the complex Kohn approach [12], which in the present context amounts to picking a real set of L^2 functions $\{\phi_i\}$, $i=1,\ldots,N$, and augmenting it with a single complex, outgoing wave continuum function ϕ_0 to produce a representation of $\langle\phi_i|H|\phi_j\rangle$, $i=0,\ldots,N$ that is complex, symmetric and generally has only complex eigenvalues. By construction, the complex function ϕ_0 behaves like an outgoing free wave, or in the case of ion scattering, an outgoing Coulomb wave. It serves to impose the proper asymptotic boundary condition so that Eq. (4) is a meaningful approximation to $G^{+}(E)$.

Consider the free-free matrix element, $\langle\phi_0^{*}|H-E|\phi_0\rangle$. (Note that the matrix element is defined without complex conjugation, which is why the function $\langle\phi_0^{*}|$ replaces the usual bra state.) Two points are to be noted. First, it is the case that the eigenvalues of H will depend on energy since the function ϕ_0 connects the wave vector $\mathbf{k}$ to E. (In the case of potential scattering, we have the relation $E=k^2/2$.) Therefore, there is nothing to be gained by diagonalizing the Hamiltonian in order to compute the resolvent. Second, we note that free-free matrix element is well defined in spite of the fact that ϕ_0 is not normalizable, since the quantity $(H-E)\phi_0$ vanishes asymptotically.

We want to consider generalizing the approach by employing several complex continuum functions, with different values of k, in a single calculation, so as to be able to span a range of energies with a single basis. This idea is not new. In fact, we suggested it some time ago in the context of computing the T matrix and found that the combination of a set of L^2 functions with several continuum functions provides a reasonable way of calculating phase shifts over a range of energies [13]. The subtlety that requires special attention in the case when several continuum functions are used or, for that matter, even one function when $E\neq k^2/2$, is how to define the overlap and kinetic energy matrix elements. The answer of course is that the matrix elements must be defined by analytic continuation from the upper half k plane. If the matrix elements are given by analytic formulas, the analytic continuation from $\mathrm{Im}(k)>0$ is given simply by those formulas. When the continuum functions are only known numerically, as is generally the case in our current implementation of the Kohn method [14], another procedure must be found.

The only matrix elements that need special attention are the free-free kinetic energy and overlap integrals, which are simple one-body elements that can be reduced to single radial integrals. These radial integrals could be carried out by performing the integration numerically on a ray in r given by $re^{i\theta}$, $0<\theta<\pi/2$, along which the free function falls off exponentially for real k [15]. However, this requires that the free functions be generated for complex arguments, which may prove inconvenient. A simpler procedure is to use ‘‘exterior complex scaling’’ [16], that is, to carry out the radial integration along the real axis from 0 to R_c and then switch to a rotated contour given by $R_c+(r-R_c)e^{i\theta}$. If R_c is sufficiently large, we can replace ϕ_0 by its asymptotic form, thus avoiding the need for numerically generating the free functions for complex r values.

It is amusing to note that these same elements can also be determined without any complex integration simply from the condition that the matrix representation of the Hamiltonian be complex symmetric. Let ϕ_0 and ϕ_0' be free functions corresponding to energies E and E'. We write the correct kinetic energy element as

$$\begin{aligned}\langle\phi_0'^{*}|T|\phi_0\rangle&=\langle\phi_0'^{*}|T-E|\phi_0\rangle+E\langle\phi_0'^{*}|\phi_0\rangle\\&=\langle\phi_0^{*}|T|\phi_0'\rangle\\&=\langle\phi_0^{*}|T-E'|\phi_0'\rangle+E'\langle\phi_0'^{*}|\phi_0\rangle,\end{aligned} \tag{5}$$

which we can use to solve for $\langle\phi_0'^{*}|\phi_0\rangle$:

$$\langle\phi_0'^{*}|\phi_0\rangle=\frac{\langle\phi_0'^{*}|T-E|\phi_0\rangle-E\langle\phi_0^{*}|T-E'|\phi_0'\rangle}{E'-E}. \tag{6}$$

The quantity $(T-E)\phi_0$ goes to zero for large r, so Eq. (6) provides a means for determining $\langle\phi_0'^{*}|\phi_0\rangle$, and then $\langle\phi_0'^{*}|T|\phi_0\rangle$ from Eq. (5), without the need for performing any complex integrations. Equation (6) is undefined for

$E=E'$, but we can apply l'Hospital's rule numerically in that case to get the diagonal elements.

We can now meaningfully approximate $\alpha^{-}(\omega)$ as

$$\alpha^{-}(\omega)=\sum_{i}\frac{\langle\Psi_0|\mu|\Phi_i\rangle\langle\Phi_i^{*}|\mu|\Psi_0\rangle}{E_i-E_0-\omega}, \tag{7}$$

where E_i and Φ_0 are the complex eigenvalues of H in the combined basis of L^2 and continuum functions.

We mentioned that the idea of combining several continuum functions into a single variational basis was originally suggested [13] in connection with the computation of the T matrix for electron scattering, which takes the form

$$\begin{aligned}T=&\langle\Phi_0|(H-E)|\Phi_0\rangle\\&-\lim_{\varepsilon\to 0}\langle\Phi_0|(H-E)\,\frac{1}{H-E-i\varepsilon}\,(H-E)|\Phi_0\rangle,\end{aligned} \tag{8}$$

where Φ_0 is the unperturbed wave function, that is, an eigenfunction of H_0, where $H=H_0+V$ and V is the interaction potential. The Green's function in Eq. (8) can be approximated by a spectral expansion of the same form we just outlined, but, in contrast to the photoabsorption expressions given by Eqs. (7) and (2), the presence of Φ_0 in the T matrix expression both in the Born and scattered wave terms on the right-hand side of Eq. (8) requires the explicit calculation of free-free matrix elements at each energy. For this reason, a spectral expansion of $G^{+}(E)$ is far less useful than in the present case of photoabsorption, where the energy dependence of the working equations is particularly trivial once the eigenvalues and eigenvectors of H have been determined.

The foregoing discussion outlines a procedure for computing the total photoabsorption cross section via Eq. (2). We will illustrate the procedure in the following section and then remark on the modifications needed to compute partial cross sections and angular distributions.

III. APPLICATION

To illustrate the procedure outlined above, we have calculated the photoionization cross section for atomic Be from threshold (ω=9.32 eV) to 13 eV. The cross section in this region [17] is dominated by a series of extremely narrow doubly excited $(2pnd),{}^1P$ Be* resonances and a broader series of $(2pns),{}^1P$ states, both converging to the $(1s^2 2p),{}^2P$ state of Be$^+$ at ω=13.28 eV.

The ground state of Be was represented by a simple configuration-interaction (CI) wave function constructed from a set of Gaussian-type orbitals. The orbital parameters are listed in Table I. The contraction coefficients for the s-type functions are those of Dunning [18]. The self-consistent field (SCF) energy of Be in this target basis is -14.5725 a.u. A $1s$ orbital was obtained from a SCF calculation on Be$^+$ ($E_{\mathrm{SCF}}=-14.2769$ a.u.) and was doubly occupied in all initial- and final-state configurations. The ground-state wave function included the configurations $(2s^2)$, $(2s2s')$, $(2s'^2)$, and $(2p^2)$. The $2s$ orbital was also obtained from the Be$^+$ SCF calculation, while the correlating $2s'$ and $2p$ orbitals are natural orbitals obtained by diagonalizing the one-particle density matrix obtained from a full CI calculation on the ground state of Be. The use of $1s$ and $2s$ ion orbitals provides a good description of the final ionized states, while the correlating natural orbitals provide the flexibility needed to give a reasonable description of the initial state. The target CI wave function we calculated has an energy of -14.6138 a.u., while the full CI value in this basis is -14.6158 a.u.

TABLE I. Gaussian basis sets used in Be photoionization calculations.

Type	Exponent	Coefficient[a]
	Target basis	
s	3630.0	0.000839
s	532.3	0.006735
s	117.8	0.035726
s	32.66	0.138635
s	10.48	0.385399
s	3.668	0.547688
s	3.668	0.213406
s	1.354	0.814692
s	0.389	1.0
s	0.1502	1.0
s	0.05241	1.0
p	2.6	1.0
p	0.5	1.0
p	0.10	1.0
p	0.032	1.0
Supplemental scattering basis		
s	0.03	1.0
s	0.015	1.0
s	0.0075	1.0
s	0.003	1.0
s	0.001	1.0
p	100.0	1.0
p	40.0	1.0
p	10.0	1.0
p	5.0	1.0
p	1.0	1.0
p	0.22	1.0
p	0.057	1.0
p	0.016	1.0
p	0.008	1.0
d	0.3	1.0
d	0.015	1.0

[a] Underlines separate contracted basis functions.

For the final ionized state calculations, the target basis was augmented with additional s-, p-, and d-type Gaussian functions, which are also listed in Table I. The ${}^1P$ final states were built from terms of the form $(1s^2 2s\ np)$, $(1s^2 2s' 2p)$, $(1s^2 2p\ ns)$, and $(1s^2 2p\ nd)$. Two independent computations of the photoabsorption cross section were carried out. In the first case, the cross section was obtained from the squared modulus of the dipole transition amplitude between the ground state and a conventional complex Kohn trial function [6] built from the above configurations and terms of the form $(1s^2 2s\phi_k)$ with numerically generated regular and outgoing wave p-wave Coulomb basis orbitals, ϕ_k, of appropri-

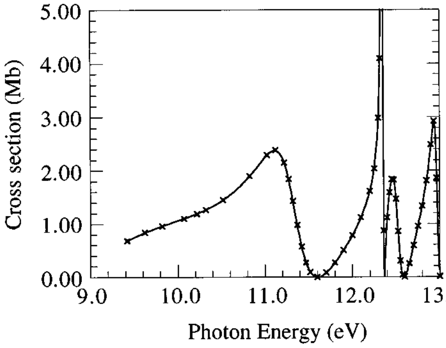

FIG. 1. Photoionization cross section of Be calculated at discrete energies using conventional Kohn wave functions (x) and from the imaginary part of the resolvent as described in text (solid line).

ate energy [14]. We also obtained the cross sections by carrying out a calculation using only two outgoing-wave basis functions corresponding to photon energies of 11.0 and 13.0 eV and using the formulas for the total cross section given by Eqs. (2) and (7). The results are displayed in Fig. 1. The two procedures yield virtually identical results. The limited Gaussian basis we used allows us to describe the first three members of the $(2p\ ns)$, ${}^1P$ resonance series, as well as the first $(2p3d)$,${}^1P$ resonance at $\omega \sim 12.4$ eV. Our results are also in reasonably good agreement with previous multichannel quantum defect theory determinations of the cross section [19–21].

IV. DISCUSSION

We have outlined a procedure for computing photoabsorption cross sections from a simple expression involving the resolvent that can be approximated by a basis set expansion. The method shares the desirable feature of R-matrix theory of being able to trivally display the energy dependence of the cross section in terms of the eigenvalues and eigenvectors of the Hamiltonian, yet unlike the R-matrix method, it does not require the matrix elements to be evaluated over a sphere of finite volume. We illustrated the method with a calculation of the photoionization cross section of Be in a region dominated by autoionizing states and showed that the structure could easily be resolved using only two energy-dependent continuum basis functions in the trial space. One may ask why this method appears to work so well. The answer lies in the fact that the energy-dependent, outgoing-wave basis functions are only needed to describe the background continuum into which the resonances decay and that this background is a slowly varying function of energy. The resonance states themselves are well described by the doubly excited configurations that are included in the CI expansion of the trial space.

One limitation of the formalism as outlined above is that it only appears capable of providing total cross sections. However, Pont and Shakeshaft [22] have addressed this point in a recent paper and have shown how Eqs. (1) and (2) can be modified to allow for the determination of partial cross sections and angular distributions. We first use the identity $(H-E)G^{+}(E)=1$ to rewrite Eq. (1) as

$$\alpha^{-}(\omega)=\langle \Psi^{1}|(H-E_{0}-\omega)|\Psi^{1}\rangle, \tag{9}$$

where

$$\Psi^{1}=\lim_{\varepsilon\to 0}\frac{1}{H-E_{0}-\omega-i\varepsilon}\,\mu|\Psi_{0}\rangle. \tag{10}$$

Pont and Shakeshaft use Green's theorem to show that the *imaginary part* of $\alpha^{-}(\omega)$ only depends on the asymptotic form of $|\Psi^{1}\rangle$. This being the case, we can introduce projection operators into Eq. (9) to produce the partial photoionization cross section for producing ions in a specific state; i.e., we can write

$$\sigma_{\Gamma}(\omega)=(4\pi\omega/c)\mathrm{Im}\langle \Psi^{1}|P_{\Gamma}(H-E_{0}-\omega)P_{\Gamma}|\Psi^{1}\rangle, \tag{11}$$

where P_{Γ} projects onto a specific ion state denoted by Γ. One can further modify the formalism to include angular functions in the projectors to extract the angular dependence of the cross section. The projection operators can only be constructed exactly for one-electron residual ions [23] and have to be approximated in other cases.

The procedure we outlined was illustrated with an atomic example, but the real utility of the method will be realized in the case of molecular photoabsorption where the choice of viable theoretical methods for *ab initio* computation is significantly more limited.

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