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Rigorous method for computing photoabsorption cross sections from a basis-set expansion*

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We present a rigorous technique, which should be applicable to both atoms and molecules, for calculating photoabsorption cross sections using square-integrable basis functions. The technique is based on the method of complex coordinates as developed by Nuttall and co-workers. In contrast to some other L^2 methods, the calculations converge directly at real energies. The method is illustrated by application to the case of atomic hydrogen.

I. INTRODUCTION

A number of studies have recently appeared which suggest that conventional bound-state techniques may be successfully employed to construct photoabsorption profiles for atoms and molecules. For several atoms and molecules accurate photoionization cross sections have been "constructed" from the results obtained from approximate bound-state calculations that employ a finite set of square-integrable (L^2) basis functions. Typically, the data provided by such a computation consist of a finite set of oscillator strengths and excitation energies, from which photoabsorption profiles are extracted. Several methods for performing the extraction have been proposed. Langhoff[1] has used the theory of moments to develop a Stieltjes-imaging procedure and has obtained good results for a number of atoms, including H, H^-, He, and Li. Broad and Reinhardt[2] developed a procedure based on a numerical analytic continuation of the frequency-dependent polarizability which they successfully applied in calculating the photoionization cross section of atomic hydrogen. The present authors and their co-workers[3] have also used this procedure to compute accurate photoionization cross sections for atomic helium and molecular hydrogen. Dalgarno and co-workers[4] have also developed an approximation scheme for obtaining photoionization cross sections from a discrete energy spectrum. In this procedure, an imaginary width is assigned to each energy, which is computed using a Fermi golden-rule-like formula.

While the above studies certainly demonstrate that the L^2 approach to photoionization can be fruitful, the fact remains that, with the exception of the work of Langhoff, the formal basis of various aspects of these methods is questionable and that, particularly in the case of numerical analytic continuation, the computational procedures employed are somewhat arbitrary.

In this paper, we develop a rigorous method for computing photoionization cross sections which employs square-integrable basis functions exclusively. The method converges directly at real energies and no secondary procedure is needed to extract the cross section. The technique is based on the method of complex coordinates developed by Nuttall and Cohen[5] for the computation of scattering amplitudes in problems involving short-range interactions. While this technique cannot be used to compute scattering amplitudes in atomic and molecular problems, which involve long-range Coulomb interactions, we will show that the method may still be used to compute photoionization cross sections. The theory is presented in Sec. II. To illustrate the method, we present numerical results for the case of atomic hydrogen, where the exact answer is known.

II. THEORY

While the method of complex coordinates has been known for some time in scattering theory as a formal tool for examining the analyticity of the S matrix,[6] it has recently served as the basis for several new computational advances. Complex-coordinate methods are presently being used in atomic and molecular problems to locate the positions and widths of scattering resonances,[7] although this method, as originally developed by Nuttall and Cohen,[5] can only be used to compute scattering amplitudes in problems involving exponentially bounded potentials.[8] We will now show how the method applies to the calculation of photoionization cross sections.

Consider the first-order equation for the wave function of an atom or molecule in the presence of an electric field,[9]

$$(H - E_0 \pm \omega)\psi^{\pm} = \mu\psi_0, \qquad (1)$$

where E_0 and ψ_0 are the stationary-state (not necessarily ground-state) energy and wave function of the target, ω is the photon frequency, and μ is the component of the dipole operator in the direction of polarization of the (unit) electric field $\hat{e}$:

$$\mu(r) \equiv \sum_{i=1}^{N} \hat{e} \cdot \vec{r}_i .$$

For our purposes, it will be sufficient to consider the negative frequency solution ψ^- only. In terms of ψ^-, the negative frequency component of the polarizability is[9]

$$\alpha^-(\omega) = \langle \psi_0 | \mu | \psi^- \rangle . \tag{2}$$

A solution to Eq. (2) may be obtained by formally inverting the operator $H - E_0 - \omega$, with the result

$$\alpha^-(\omega) = \langle \psi_0 | \mu \frac{1}{H - E_0 - \omega - i\epsilon} \mu | \psi_0 \rangle , \tag{3}$$

which may also be written as

$$\alpha^-(\omega) = \sum_i \frac{|\langle \psi_0 | \mu | \psi_i \rangle|^2}{E_i - E_0 - \omega} + \int \frac{|\langle \psi_0 | \mu | \psi_E \rangle|^2 \, dE}{E - E_0 - \omega - i\epsilon} . \tag{4}$$

In Eq. (4), the sums and integrals go over all optically allowed bound and continuum target states with wave functions and energies by ψ_i, E_i and ψ_E, E, respectively.

For frequencies above the first ionization potential of the target, the integral in Eq. (4) is complex valued, with imaginary part given by

$$\mathrm{Im}(\alpha^-(\omega)) = \pi |\langle \psi_0 | \mu | \psi_\omega \rangle|^2 . \tag{5}$$

Thus from $\mathrm{Im}(\alpha^-(\omega))$ we can construct the continuum oscillator strength, $dg/d\omega$,

$$\frac{dg}{d\omega} = 2 \frac{\omega}{\pi} \mathrm{Im}(\alpha^-(\omega)), \tag{6}$$

or, equivalently, the photoionization cross section

$$\sigma(\omega) = 4(\pi/c)\omega \, \mathrm{Im}(\alpha^-(\omega)). \tag{7}$$

We note that the L^2 methods referred to previously all imply some discrete approximation to $\alpha^-(\omega)$ in Eq. (4) of the form

$$\sum_j \frac{\langle \psi_0 | \mu | \psi_j \rangle \langle \psi_j | \mu | \psi_0 \rangle}{E_j - E_0 - \omega} .$$

However, the pole structure of this expression obviously does not represent the correct analytic structure of $\alpha^-(\omega)$ in the continuum and consequently some secondary procedure must be employed to obtain meaningful results from such an expression.

The method of complex coordinates, however, can be used to obtain these results directly. From Eq. (2), we have

$$\alpha^-(\omega) = \int \psi_0^*(r_1, \ldots, r_N) \mu(r) \times \psi^-(r_1, \ldots, r_N) \prod_{i=1}^{N} d^3 r_i . \tag{8}$$

From now on we use the symbol r to refer collectively to the coordinates of all electrons.

We next perform a contour distortion in the *radial* parts of the above integral and carry out the integrations along the rotated paths defined by $\theta = e^{i\varphi}$, $\varphi > 0$. Provided ψ_0 and ψ^- decrease sufficiently rapidly at infinity, Cauchy's theorem guarantees that the numerical value of the integral will be unchanged. Assuming for the moment that this is the case, we obtain the result

$$\alpha_\theta^-(\omega) = \theta^{3N} \int \psi_0^\dagger(r\theta) \mu(r\theta) \psi^-(r\theta) \, d^3 r_i . \tag{9}$$

The conjugate function $\psi_0^\dagger$ is defined by taking the complex conjugate of all angular functions, but not of the radial coordinates.[10]

Since $\psi_0(r)$ is a bound state and consequently falls off exponentially as any $r_i \to \infty$, we can always find a range of values of $\varphi > 0$ such that $\psi_0(r\theta)$ still decreases exponentially. Furthermore, this same condition guarantees that $\psi^-(r\theta)$ is also square-integrable.[5] $\psi^-(r\theta)$, which satisfies the differential equation

$$(H(r\theta) - E_0 - \omega)\psi^-(r\theta) = \mu(r\theta)\psi_0(r\theta), \tag{10}$$

is again solved formally by inverting the operator $(H(r\theta) - E_0 - \omega)$, yielding for $\alpha_\theta^-(\omega)$,

$$\alpha_\theta^-(\omega) = \theta^{3N} \int \psi_0^\dagger(r\theta) \mu(r\theta) \frac{1}{H(r\theta) - E_0 - \omega} \times \mu(r\theta) \psi_0(r\theta) \, d^3 r . \tag{11}$$

In contrast to $(H - E_0 - \omega - i\epsilon)^{-1}$, a discrete spectral representation of the operator $[H(r_i\theta) - E - \omega]^{-1}$ is meaningful for all real ω and converges as the basis set is improved. This suggests the following prescription for calculating the photoionization cross section of an atom or molecule:

(a) Perform the transformation $r_i \to r_i\theta$ on all the coordinates in the Hamiltonian.

(b) Form a matrix representation of the Hamiltonian in a discrete set of basis functions. Note that for atomic and molecular systems, the coordinate rotation is particularly trivial. The kinetic-energy matrix elements are simply multiplied by θ^{*2} and all other matrix elements by θ^*; no new types of matrix elements need be computed at this point.[7]

(c) Compute the matrix inverse $[\underline{H}(r\theta) - E_0 - \omega]^{-1}$. Note that $\underline{H}(r\theta)$ is a non-Hermitian matrix. If real basis functions are used, it will be complex symmetric. If solutions are desired for many values of ω, it may be most expedient to diagonalize $\underline{H}(r\theta)$ and form

$$\frac{1}{\underline{H}(r\theta) - E_0 - \omega} = \frac{\psi_i \psi_i^\dagger}{E_i - E_0 - \omega} . \tag{12}$$

The complex eigenvalues E_i can also be used in connection with a resonance search.[7] Note that the conjugate vectors $\psi_i^\dagger$ are formed by complex-conjugating angular variables only and *not radial variables*.

(d) Form $\alpha_\theta^-(\omega)$ from the expression

$$\alpha_\theta^-(\omega) = \sum_i \theta^{3N} \frac{\int \psi_0^\dagger(r\theta)\mu(r\theta)\psi_i(r) \int \psi_i^\dagger(r)\mu(r\theta)\psi_0(r\theta)}{E_i - E_0 - \omega}. \tag{13}$$

It is only at this last stage that new types of matrix elements are needed. In evaluating the dipole-matrix elements of Eq. (13), the basis functions referring to ψ_0 contain complex coordinates while the vectors ψ_i are linear combinations (the coefficients are complex!) of unrotated basis states. However, since the dipole-matrix elements are simply one-body matrix elements, the necessary modifications could be made in any standard bound-state program with little trouble.

(e) Compute the photoionization cross section from the expression

$$\sigma(\omega) = 4(\pi/c)\omega \, \mathrm{Im}(\alpha_\theta^-(\omega)).$$

In Sec. III we summarize the results of a numerical application of this method to atomic hydrogen.

III. APPLICATION: ATOMIC HYDROGEN

We have tested the method outlined above by applying it to the case of atomic hydrogen. The transformation $r \to re^{i\varphi}$ was applied to the radial hydrogen Hamiltonian for $l = 1$ and the resulting operator diagonalized in basis set of N functions of the form $r^n e^{-\lambda r/2}$, $n = 1, \ldots, N$ with $\lambda = 1.8$, which is similar to the basis set used by Broad and Reinhardt for this problem.[2] Table I shows the continuum oscillator strengths obtained for a rotation angle of 30° and varying numbers of basis functions. We have also given the exact answer for hydrogen which is known in closed form[11]

$$\frac{dg}{d\omega} = \frac{\frac{16}{3} \exp[-4(2\omega-1)^{-1/2} \tan^{-1}(2\omega-1)^{1/2}]}{\omega^4\{1 - \exp[-2\pi(2\omega-1)^{-1/2}]\}}.$$

TABLE I. Continuum oscillator strengths for atomic hydrogen.[a]

ω[a]	N[b] = 5	$N = 10$	$N = 15$	Exact
0.6	0.9461	0.9568	0.9568	0.9569
0.8	0.4361	0.4331	0.4332	0.4332
1.0	0.2322	0.2308	0.2309	0.2309
1.2	0.1371	0.1368	0.1368	0.1369
1.4	0.0870	0.0874	0.0875	0.0875
1.6	0.0579	0.0591	0.0591	0.0591
1.8	0.0399	0.0417	0.0417	0.0417
2.0	0.0282	0.0304	0.0305	0.0305

[a] Frequencies and oscillator strengths are given in atomic units.

[b] N refers to the number of functions used to diagonalize the Hamiltonian. Basis functions used were of the form $r^n e^{-\lambda r/2}$, $n = 1, \ldots, N$. For these calculations we chose $\lambda = 1.8$ and a rotation angle of 30°.

The results indicate the satisfactory answers may be obtained with as few as five basis functions.

IV. CONCLUSION

We have outlined a rigorous method for computing atomic and molecular photoabsorption cross sections using discrete basis functions and demonstrated the procedure for the case of atomic hydrogen. The method should be of considerable utility in application to more complex systems and its implementation can be achieved by making relatively minor changes to existing many-body or configuration-interaction bound-state programs.

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