

Calculation of helium photoionization in the random-phase approximation using square-integrable basis functions*

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The photoionization cross section of helium is calculated by a numerical analytic continuation of the frequency-dependent polarizability. Approximate values of the polarizability are obtained by an application of the equations-of-motion method. The entire calculation is performed without the use of continuum basis functions. The calculated cross sections agree well with the observed values.

I. INTRODUCTION

There has been much interest recently in the application of bound-state computational techniques to problems associated with the continuous spectrum of an operator. The efforts of various workers have shown that physical information can often be extracted from the discrete representation obtained by projection of the appropriate Hamiltonian onto a finite set of square-integrable basis functions. Such techniques have been used by Hazi and Taylor in the location of scattering resonances,¹ by Schwartz and Schlessinger,² by Nuttall and co-worker³ in calculations of the T matrix, and by Reinhardt and co-workers⁴ in applications of the Fredholm method to electron-atom scattering problems. Much of this work has shown that the discrete representation of an operator, while not directly useful at physical energies in the continuum, often provides an entirely adequate representation of the operator for complex values of the energy. The technique of numerical analytic continuation⁵ can then be used to return to the real energy axis where physical information is desired. The essential point is that the L^2 methods completely obviate the need for constructing continuum solutions of the wave equation, which for heavier atoms and even small molecules can be a formidable computational undertaking.

Recent work by Broad and Reinhardt⁶ suggests that numerical analytic continuation can also be used to extract photoionization cross sections from discrete representations of the frequency-dependent polarizability calculated in the complex plane. The Stieltjes imaging technique of Langhoff⁷ provides an alternative approach to constructing photoionization cross sections from a discrete set of transition energies and oscillator strengths. However, the justification for Langhoff's simple prescription apparently depends on

satisfying $2n$ energy weighted sum rules when an n -point discrete spectrum is used.

In this work we apply the method of Broad and Reinhardt to the discrete representation of the frequency-dependent polarizability of helium in the random phase approximation (RPA). For purposes of comparison we also compute the photoionization cross section by Stieltjes imaging. It is important to point out that unlike the RPA calculations of photoionization by Amus'ya *et al.*,⁸ Jamieson,⁹ and Altick and Glassgold,¹⁰ our calculation employs square-integrable basis functions exclusively. Thus the techniques used here can be easily extended to the molecular case.

The outline of this paper is as follows: in Sec. II we briefly review the numerical method of Broad and Reinhardt and the linearized equations of motion method (RPA). In Sec. III we present our numerical results and compare them with experiment. Section IV contains a brief discussion.

II. THEORY

A. Photoionization

The frequency-dependent polarizability $\alpha(z)$ of an atom or molecule is given by the formal expression¹¹

$$\alpha(z) = \sum_{i \neq 0} \frac{f_{0i}}{\omega_{0i}^2 - z^2} + \int_{\epsilon_1}^{\infty} \frac{g(\epsilon) d\epsilon}{\epsilon^2 - z^2}, \quad (1)$$

where ω_{0i} , f_{0i} , and $g(\epsilon)$ are the transition frequencies and the bound and continuum oscillator strengths, respectively, and ϵ_1 is the first ionization threshold of the system. Taking the limit $z \rightarrow \omega + i\eta$ in Eq. (1) yields

$$\alpha(\omega) = \sum_{i \neq 0} \frac{f_{0i}}{\omega_{0i}^2 - \omega^2} + \mathcal{P} \int_{\epsilon_1}^{\infty} \frac{g(\epsilon) d\epsilon}{\epsilon^2 - \omega^2} + \frac{i\pi g(\omega)}{2\omega} \quad (2)$$

and thus the result¹²

$$\alpha(\omega) = \lim_{\eta \rightarrow 0} \frac{4\pi\omega}{C} \text{Im}[\alpha(\omega + i\eta)], \quad \omega > \epsilon_1 \quad (3)$$

for the photoionization cross section.

In this work, the polarizability is first approximated by a finite sum

$$\alpha(z) \approx \sum_{i=1}^n \frac{\tilde{f}_{0i}}{\tilde{\omega}_{0i}^2 - z^2}. \quad (4)$$

Equation (4) can be viewed as a quadrature-like approximation¹³ to the frequency-dependent polarizability and might thus be expected to provide an adequate representation of $\alpha(z)$ for complex values of z away from the poles ω_{0i} . This being the case, we construct a low-order rational-fraction representation² of the polarizability by fitting it to the approximate expression (4) at a number of points in the complex plane. The rational fraction can then be used to obtain smooth values of $\alpha(\omega)$, and hence $\sigma(\omega)$, for real energies where the original finite approximation is invalid. The rational-fraction representation

$$R_{M,M} = \frac{\sum_{i=0}^M P_i z^i}{1 + \sum_{i=1}^M Q_i z^i} \quad (5)$$

of the polarizability is obtained by matching Eq. (5) to $\alpha(z_i)$ at $2M+1$ complex values of z_i . In actual computations, a continued fraction representation of $R_{M,M}$ is used, whose coefficients are calculated recursively.¹⁴

It is important to realize that $\alpha(z)$ in the form of Eq. (4) is itself a rational fraction $R_{2n-2,2n}$. Consequently, in fitting $\alpha(z)$ to a rational fraction in the complex plane, it is essential to choose a low-order rational fraction so as not to reproduce the pole behavior of the finite-sum approximation on the real axis. Since there is no *a priori* rule for choosing the order of the rational fraction or the fitting points, it is important to vary both of these in any numerical application to check that the continued results are stable.

B. Equations-of-motion method

A finite set of oscillator strengths and transition frequencies, needed to obtain a discrete representation of $\alpha(z)$, was generated by solving the equations of motion for helium in the simplest approximation, the usual random phase approximation. The equations-of-motion method has been discussed previously,¹⁵ and only a brief summary of the theory limited to the random phase approximation will be given here. The operator O_λ^\dagger which generates excited state $|\lambda\rangle$ from the ground state $|0\rangle$ can be shown to be exactly a solution of the equation of motion¹⁶

$$\langle 0 | [\delta O_\lambda, H, O_\lambda^\dagger] | 0 \rangle = \omega_\lambda \langle 0 | [\delta O_\lambda, O_\lambda^\dagger] | 0 \rangle. \quad (6)$$

TABLE I. Transition energies and oscillator strengths for He in the [12S/8P] and [10S/13P] calculations. The quantities in brackets refer to the number of Gaussian basis functions used in solving the RPA equations. Energies are given in atomic units.

[10S/13P]		[12S/8P]	
f_{0i}	ω_{0i}	f_{0i}	ω_{0i}
0.2520	0.7970	0.2520	0.7970
0.0705	0.8636	0.0705	0.8636
0.0288	0.8874	0.0528	0.8909
0.0372	0.9008	0.1338	0.9369
0.1290	0.9429	0.3939	1.086
0.3834	1.089	0.7080	1.661
0.6525	1.628	0.3696	4.214
0.3372	3.247	0.0210	13.72
0.0873	6.936		
0.0207	16.29		
0.0018	44.73		
0.0006	135.0		
0.0	431.5		

In Eq. (6), ω_λ is the excitation frequency, and the double commutator is defined as

$$2[A, B, C] = [[A, B], C] + [A, [B, C]]. \quad (7)$$

If O_λ^\dagger is restricted to single particle-hole components, it has the form¹⁶

$$O_\lambda^\dagger(SM) = \sum_{m\gamma} [Y_{m\gamma}(\lambda) C_{m\gamma}^\dagger(SM) - Z_{m\gamma}(\lambda) C_{m\gamma}(\bar{S}\bar{M})], \quad (8)$$

where $C_{m\gamma}^\dagger(SM)$ and $C_{m\gamma}(\bar{S}\bar{M})$ are spin-adapted particle-hole creation and annihilation operators corresponding to spin S and projection M . Equation (6) then becomes a matrix equation for the amplitudes $\{Y_{m\gamma}(\lambda)\}$ and $\{Z_{m\gamma}(\lambda)\}$

$$\begin{pmatrix} \underline{A} & \underline{B} \\ -\underline{B}^* & -\underline{A}^* \end{pmatrix} \begin{pmatrix} Y(\lambda) \\ Z(\lambda) \end{pmatrix} = \omega_\lambda \begin{bmatrix} \underline{D} & 0 \\ 0 & \underline{D} \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix}. \quad (9)$$

The matrices \underline{A} , \underline{B} , and \underline{D} are given elsewhere.¹⁵

TABLE II. Energy weighted oscillator strength sums of He. The 8- and 13-term RPA results are compared with the variational results of Chan and Dalgarno and the accurate results of Pekeris (see Ref. 19). Atomic units are used throughout. k refers to the power of ω_{0i} in the sum $\sum_i f_{0i} \omega_{0i}^k$.

k	8-term RPA	13-term RPA	Chan and Dalgarno	"Accurate"
-6	1.730	1.731	1.9840	2.0672
-4	1.386	1.386	1.520	1.5616
-2	1.322	1.322	1.3788	1.3912
-1	1.478	1.479	1.5046	1.5050
0	2.001	2.000	2.0	2.0
1	3.883	4.121	3.91	4.35
2	13.306	30.345	13.32	30.32

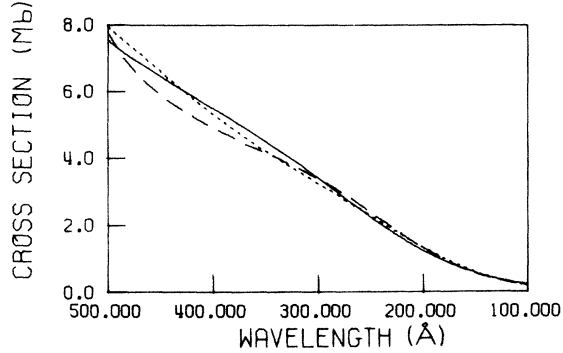


FIG. 1. Photoionization cross section of helium in the eight-pole RPA calculations. The curves show the results of three different choices of fitting points used for construction of the rational fraction. Seven fitting points were chosen in each case with $\text{Re}(z_i) = (\omega_{0i+1} + \omega_{0i})/2$. The choices for $\text{Im}(z_i)$ were: $2(\omega_{0i+1} - \omega_{0i})$, solid curve; $3(\omega_{0i+1} - \omega_{0i})$, dashed curve; and $4(\omega_{0i+1} - \omega_{0i})$, dotted curve. Cross sections are given in units of Mb, and wavelengths are in Å.

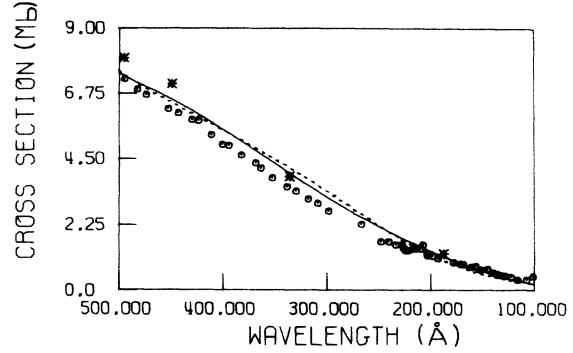


FIG. 2. Comparison of calculated photoionization cross section of helium with the experimental results of Samson (©). The solid and dashed curves are the results of the 13- and 8-pole RPA calculations, respectively. In each case, the fitting points for the rational fraction were chosen as $z_i = ((\omega_{0i+1} + \omega_{0i})/2, i2(\omega_{0i+1} - \omega_{0i}))$. We have also plotted the Stieltjes-imaging results (*) for the [10S/13P] RPA calculation. Cross sections are in Mb and wavelengths are in Å.

If $|0\rangle$ is taken to be the Hartree-Fock ground state, \underline{D} becomes the unit matrix and the familiar RPA matrix equation is obtained. In the RPA the dipole transition moment between excited state $|\lambda\rangle$ and ground state $|0\rangle$ for an N -electron system is given by

$$M_{0\lambda} = \langle 0 | \sum_{i=1}^N \vec{r}_i | \lambda \rangle$$

$$= \sqrt{2} \sum_{m\gamma} M_{m\gamma}^0 (Y_{m\gamma}(\lambda)^\dagger Z_{m\gamma}(\lambda)) . \quad (10)$$

where $M_{m\gamma}^0$ is the matrix element of the position vector \vec{r} between particle state m and hole state γ .

The RPA provides a particularly convenient method for constructing a finite representation of the frequency-dependent polarizability. The dipole length and velocity formulas for the oscillator strength are equivalent in this approximation and the f -sum rule is satisfied.¹⁷

III. NUMERICAL RESULTS

The RPA equations were solved using [12S/8P] and [10S/13P] sets of Gaussian basis functions (see for example, Ref. 18). The transition energies and oscillator strengths from these calculations are given in Table I. In each case the oscillator strengths of the two lowest bound solutions of P symmetry agree with experiment to better than 10%. We have also evaluated the energy weighted sums $S(k) = \sum_{i=1}^N f_{0i}(\omega_{0i})^k$ for $-6 \leq k \leq 2$, and these are shown in Table II along with the accurate values of Pekeris and the calculated values

of Chan and Dalgarno (four-term variational calculation).¹⁹ Figure 1 shows photoionization cross section for the eight-pole case for three different choices of the fitting points. These curves demonstrate that, over a fairly broad region in the complex plane, the calculated cross sections are relatively insensitive to the points used to construct the rational fraction. A similar study of the results in the 13-pole case led to cross sections which were indistinguishable on the scale of Fig. 1. Figure 2 compares the results of our 8- and 13-pole calculations with the experimental cross sections of Samson.²⁰ For comparison we have also plotted the values of the photoionization cross section obtained by Stieltjes-imaging⁸ the 13-pole results.

IV. DISCUSSION

The results given here again indicate that it is not necessary to employ continuum basis functions in photoionization calculations. Preliminary results also indicate that this is true in the molecular case, although several modifications of the analytic-continuation method are necessary. These developments will be discussed in future publications.

We should like to make a final point before concluding. We have worked with the expression for the full polarizability

$$\int \frac{g(\epsilon)}{\epsilon^2 - z^2} d\epsilon$$

which, in the limit $z \rightarrow \omega + i\eta$, has imaginary part

proportional to the photoionization cross section. One could work equally well with the positive frequency contribution to the polarizability

$$\frac{1}{2} \int \frac{g(\epsilon) d\epsilon}{\epsilon - z}.$$

The point is that the technique of numerical continuation allows one to make finite quadrature-like approximations to these integrals and indirectly pick up the residue on the real energy axis. Bearing this in mind, one could, in principle, substitute the generalized oscillator strengths²¹ in Eq. (1), and analytic continuation could then be

used to find values of the Born cross section in the continuum. One could, in principle, construct the entire Bethe surface²¹ of an atom or molecule in such a fashion. But in practice one would probably need larger basis sets than were used here, since all angular momentum states would contribute to the generalization of Eq. (1).

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