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Complex-basis-function calculations of resolvent matrix elements: Molecular photoionization

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Procedures for computing molecular photoabsorption cross sections via finite expansions in sets of L^2 complex basis functions are discussed. Two recently proposed schemes for analytically continuing a matrix representation of the Born-Oppenheimer Hamiltonian are investigated. Both of these matrix analytic continuations are used to compute the parallel component of the photoionization cross section for $H_2{}^+$. It is found that to obtain numerically stable results it is necessary to use complex-basis functions which are capable of describing cusps in the molecular wave function at complex values of the coordinates. The application of this technique to larger molecules is also discussed.

I. INTRODUCTION

The method of complex scaling has proved useful in a number of applications to the study of atomic resonance phenomena and continues to attract considerable attention in the current literature.[1] Moreover, several novel applications suggest that the method may have a wider range of applicability than the class of dilatation analytic Hamiltonians for which the theory was originally developed.[2] In this connection, recent theoretical and computational studies on extending the method of complex scaling to molecular problems within the Born-Oppenheimer framework are particularly noteworthy since they point to the possibility of avoiding detailed scattering calculations which, for molecules, can be intractable.[3-5]

Two computational techniques have been proposed to date for extending complex scaling techniques to molecular resonance problems. In an earlier study, McCurdy and Rescigno[3] proposed the use of ordinary floating Gaussian basis functions which are made complex by simply scaling the orbital exponents by a phase factor. It was argued that such functions, when used to form a matrix representation of the Born-Oppenheimer Hamiltonian with a complex-valued scalar product, would effectively provide an asymptotic scaling of the electronic coordinates and that such a scaling would be sufficient to render a resonance eigenfunction L^2; this supposition was supported by several illustrative calculations. More recently, Moiseyev and Corcoran[4] have described a procedure which superficially appears to be identical to the transformation $r \rightarrow \lambda r e^{i\phi}$ that can be applied to the electronic coordinates of a dilatation analytic Hamiltonian. This simple analogy is complicated, however, by the fact that the branch-point singularities in the electron-nuclear attraction terms of the Born-Oppenheimer Hamiltonian render it a nonanalytic function of electronic coordinates. In addition to these numerical studies, the formal work of Simon[5] establishes that complex scaling in the Born-Oppenheimer picture can be put on firm mathematical ground through the use of what Simon[5] calls the method of "exterior complex scaling" in which the magnitudes of all electronic coordinates are only scaled outside a sphere which is large enough to enclose all the nuclei.

The most recent development in this area is the observation by McCurdy[6] that the method of Moiseyev and Corcoran[4] can be formally related to Simon's exterior complex scaling. Having established this connection, McCurdy also shows that the Moiseyev-Corcoran[4] procedure can be used to calculate the matrix elements of the resolvent which are needed to evaluate photoionization cross sections for molecules, in analogy with a similar procedure used in atomic problems.[7] In the present paper, we establish a connection between the McCurdy-Rescigno[3] and Moiseyev-Corcoran[4] procedures. Their relative utility as computational techniques is assessed by carrying out a comparative study of the two methods in connection with an evaluation of the photoionization cross section of $H_2{}^+$. We show that the Rescigno-McCurdy procedure provides far more stable and reliable results for a given choice of basis functions and we provide an explanation for the evidently slower rate of convergence of the Moiseyev-Corcoran[4] procedure. The fact that this increased stability is also observed in bound-state energies indicates that the McCurdy-Rescigno[3] method will also be found to give more stable results for resonance eigenvalues. We conclude with some remarks about the possible use of these techniques in applications involving larger molecules.

II. THEORETICAL DEVELOPMENT

Complex scaling techniques have been applied to the calculation of atomic photoabsorption cross sections[7] by making use of the fact that the cross section $\sigma(\omega)$ can be expressed as a matrix element of the resolvent between square integrable functions:

$$\sigma(\omega) \overset{\lim}{\underset{\epsilon\to 0}{=}} \frac{4\pi\omega}{c} \operatorname{Im}\left\langle \psi_0 \middle| \mu \frac{1}{H-E_0-\omega-i\epsilon} \mu \middle| \psi_0 \right\rangle, \quad (1)$$

where ψ_0 is the wave function for the atom in its initial state with energy E_0, μ is the dipole operator, and ω is the photon frequency. Under the transformation $r \to \theta r$, $\theta = \lambda e^{i\phi}$ for all electronic coordinates, the continuous spectrum of the atomic Hamiltonian is rotated off the real axis. This makes it possible to obtain convergent approximations to Eq. (1) by inverting a finite matrix representation of the scaled Hamiltonian obtained over a set of normalizable functions, whereas such a representation could not be used directly at real energies in the continuum for the unscaled Hamiltonian.[7]

Difficulties in extending complex scaling techniques to molecular problems in the Born-Oppenheimer approximation arise because the nuclear attraction terms

$$V_{\text{nuc}} = \sum_{i,j} \frac{-Z_j}{|\vec{r}_i - \vec{R}_j|} \quad (2)$$

do not simply scale under the transformation $r \to \theta r$, each term having a circle of square-root branch points[5,6] with $\vec{r}_i$ satisfying

$$\lambda |\vec{r}_i| = |\vec{R}_j| ,$$
$$\hat{r}_i \cdot \hat{R}_j = \cos\phi .$$

Simon[5] has shown that one solution to this problem is to scale the magnitudes of all electronic coordinates outside a sphere of radius R_0 large enough to enclose all the nuclei. Simon transforms the electronic coordinates according to $r \to R(r)$ where

$$R(r) = \begin{cases} r, & 0 < r \leqslant R_0 \\ R_0 + \lambda e^{i\phi}(r - R_0), & R_0 \leqslant r \end{cases} \quad (3)$$

and has shown that the spectrum of the Hamiltonian under this transformation is the same as that obtained for atoms under the more familiar complex scaling transformation.

There have been as yet no attempts to implement the original form of Simon's exterior complex scaling computationally. The two numerical procedures which have been proposed are based on different analytic continuations of the *matrix elements* of the Born-Oppenheimer Hamiltonian in a basis of Cartesian Gaussian functions. Moiseyev and Corcoran[4] proposed a procedure which superficially appears to be the same as the usual complex scaling method used for atoms.[1] Consider the transformation $r \to \theta r$, $\theta = \lambda e^{\eta}$, where λ and η are real. If we then define the matrix $H_{\alpha\beta}(\theta)$ with respect to the Gaussian basis functions χ as (specializing the notation to a one-electron molecule for simplicity)

$$H_{\alpha\beta}(\theta) = \int d^3r \chi_\alpha(\vec{r}) H(\theta) \chi_\beta(\vec{r}) , \quad (4)$$

it can be shown that these matrix elements, which can all be evaluated in closed form, are entire functions of θ.[6,8] Moiseyev and Corcoran[4] simply evaluated Eq. (4) for $\eta = i\phi$ and found that the computed eigenvalues behaved as expected under the usual complex scaling transformation.

McCurdy[6] has pointed out that this procedure is not the same as forming matrix elements of the scaled Born-Oppenheimer Hamiltonian $H(\theta)$ for complex values of θ, but can be interpreted as a matrix representation of the exterior scaled Hamiltonian with respect to complex basis functions. The reader is referred to Ref. 6 for details of the argument; only a brief recapitulation is given here. Specifically, we have the identity

$$H_{\alpha,\beta}(\theta) \equiv \int d^3r \frac{dc(r)}{dr} \left(\frac{c(r)}{r}\right)^2 \times \chi_\alpha(c(r)\hat{r}) H_{R_0}(\theta) \chi_\beta(c(r)\hat{r}) , \quad (5)$$

where $H_{R_0}(\theta)$ is the exterior scaled Hamiltonian and $\chi_\alpha(c(r)r)$ is the (complex) basis function evaluated along the contour defined by

$$c(r) = \begin{cases} 1/\lambda e^{-i\phi} r , & 0 \leqslant r \leqslant R_0 \\ 1/\lambda e^{-i\phi} R_0 + (r - R_0) , & R_0 \leqslant r . \end{cases} \quad (6)$$

Note that the quotient $R(r)/c(r) = \lambda e^{i\phi}$ is independent of R_0. Also, the weighting function $[dc(r)/dr][c(r)/r]^2$ appearing in Eq. (5) does not change this interpretation, and we can obtain the secular equation solved by Moiseyev and Corcoran[4] with the matrix $H_{\alpha\beta}(\theta)$ by solving the Schrödinger equation for Simon's[5] exterior scaled Hamiltonian using a Galerkin approximation. See Ref. 6 for details of this derivation.

The same arguments that lead to the derivation of Eq. (5) can be used to derive an approximation to the resolvent matrix element [Eq. (1)] that gives the photoionization cross section.[6] We can rewrite Eq. (1) as

$$\sigma(\omega) = (4\pi\omega/c)\,\mathrm{Im}\,I(\omega)\,,$$
$$I(\omega) = -\int d^3r\, d^3r' f(\vec{r})G(\omega,\vec{r},\vec{r}\,')f(\vec{r}\,')\,, \tag{7}$$

where

$$f(\vec{r}) = \mu(\vec{r})\,\psi_0(\vec{r})$$

and $G(\omega,\vec{r},\vec{r}\,')$ is the resolvent operator $G(\omega,\vec{r},\vec{r}\,') = (E_0+\omega-H+i\epsilon)^{-1}$.

The integration paths in Eq. (7) are first distorted onto the contour $R(r)$ and the scaled resolvent is then approximated by forming the matrix inverse $[E_0+\omega-H_{R_0}(\theta)]^{-1}$ over the set of complex functions $\{\chi_\alpha(c(r)\hat{r})\}$. The resulting expression for $I(\omega)$ is[6]

$$I(\omega) \approx -\theta^3\, \vec{f}\,(\underline{E_0+\omega-H})_\theta^{-1}\vec{f}\,, \tag{8}$$

where the inverse $(\underline{E_0+\omega-H})_\theta^{-1}$ is simply formed from the analytically continued matrix elements $H_{\alpha,\beta}(\theta)$ of Eq. (4) and the elements of $\vec{f}$ are approximated by

$$f_\alpha = \theta^{-3}\sum_\beta d_\beta \int d^3r\, \chi_\beta(\vec{r})\mu(\vec{r}\theta)\,\chi_\alpha(\vec{r})\,. \tag{9}$$

The expansion coefficients d_β in Eq. (9) make up the eigenvector corresponding to ψ_0 and are determined by diagonalizing $H_{\alpha,\beta}(\theta)$ over basis functions of the initial-state symmetry. The matrix inverse $(\underline{E_0+\omega-H})_\theta^{-1}$ is then constructed over a set of functions of opposite parity. It is important to note that the final set of working equations [Eqs. (4), (8), and (9)] only involve the complex matrix elements $H_{\alpha,\beta}(\theta)$ and transition moment elements between the basis functions $\chi_\alpha(r)$. The contour integrations along the paths $R(r)$ and $c(r)$ are a formal device used to motivate the final set of equations and are not needed in practice.[6]

The numerical scheme proposed by McCurdy and Rescigno[3] exploits the fact that it is the asymptotic form of the eigenfunctions of the Hamiltonian which determine the modification of the spectrum under complex scaling. The procedure is to use basis functions which effectively scale $\vec{r}$ by θ asymptotically while avoiding the nonanalyticity problem at the nuclear centers. This is accomplished by forming a matrix representation of the *unscaled* Born-Oppenheimer Hamiltonian in a basis set of *complex Cartesian* Gaussians of the form

$$\psi_{lmn}(\alpha,\vec{r},\vec{A}) = N_{lmn}(x-A_x)^l(y-A_y)^m(z-A_z)^n \times e^{-\alpha\theta^{-2}(\vec{r}-\vec{A})^2}. \tag{10}$$

It was argued[3] that using such a basis is equivalent to using rotated coordinates in the Hamiltonian asymptotically.

It is instructive to compare the behavior of the analytically continued matrix elements in the Moiseyev-Corcoran[4] and McCurdy-Rescigno[3] procedures, particularly the matrix elements of the nuclear attraction potential. We will consider a matrix element of one term of the nuclear potential between two S-type Gaussians [$l=m=n=0$ in Eq. (10)] both centered at position $\vec{A}$ (Ref. 8):

$$I = \left[\frac{2\alpha}{\pi}\right]^{3/4}\left[\frac{2\beta}{\pi}\right]^{3/4}\int d^3r\, e^{-\alpha(\vec{r}-\vec{A})^2}\frac{1}{|\vec{r}-\vec{R}|}e^{-\beta(\vec{r}-\vec{A})^2}$$
$$= \left[\frac{32}{\pi}\right]^{1/2}\frac{(\alpha\beta)^{3/4}}{(\alpha+\beta)}F_0((\alpha+\beta)(\vec{R}-\vec{A})^2)\,, \tag{11}$$

where $F_0(z)$ is the entire function of z,

$$F_0(z) = \tfrac{1}{2}(\pi/z)^{1/2}\,\mathrm{erf}(z)\,.$$

The Moiseyev-Corcoran procedure[4] replaces $(\vec{r}-\vec{R})^2$ with $(\vec{r}\theta-\vec{R})^2$ in Eq. (11) and obtains a formula for I by factoring θ^{-1} out of the integrand. Evaluating the result at complex θ gives

$$I^{\mathrm{MC}} = \frac{e^{-i\phi}}{\lambda}\left[\frac{32}{\pi}\right]^{1/2}\frac{(\alpha\beta)^{3/4}}{(\alpha+\beta)} \times F_0\left((\alpha+\beta)\left[\frac{\vec{R}e^{-i\phi}}{\lambda}-\vec{A}\right]^2\right). \tag{12}$$

In the McCurdy-Rescigno procedure, we simply multiply α and β in Eq. (11) by θ^{-2}, giving

$$I^{\mathrm{MR}} = \frac{e^{-i\phi}}{\lambda}\left[\frac{32}{\pi}\right]^{1/2}\frac{(\alpha\beta)^{3/4}}{(\alpha+\beta)} \times F_0\left(\frac{(\alpha+\beta)e^{-2i\phi}}{\lambda^2}(\vec{R}-\vec{A})^2\right). \tag{13}$$

It is now clear from comparing Eqs. (12) and (13) that the McCurdy-Rescigno procedure can be related to the Moiseyev-Corcoran procedure; if the basis functions are simply shifted from center $\vec{A}$ to $\vec{A}\theta^{-1}$ in the latter, it reduces to the McCurdy-Rescigno prescription. In fact, the entire argument of Ref. 6 showing how the Moiseyev and Corcoran[4] procedure is related to Simon's exterior scaling,[5] is applicable to the case when $\vec{A}$ is changed to $\vec{A}\theta^{-1}$, and therefore the McCurdy-Rescigno procedure for analytically continuing the matrix elements of the Hamiltonian is equivalent to exterior scaling in the sense of our Eq. (5).

Note that as the orbital exponents α and β become small, I^{MC} and I^{MR} limit to the same numerical value since $\lim_{z\to 0}F_0(z)\to 1$. Since the matrix elements become independent of the orbital center in this limit (diffuse basis functions), it does not matter whether one associates a factor of $e^{-2i\phi}/\lambda^2$ with the orbital exponents or a factor of $e^{-i\phi}/\lambda$ with the electronic coordinates r. Furthermore, since the asymptotic behavior of the eigenfunctions is determined by the most diffuse functions, it is clear that both procedures should yield the same spectrum in the limit of a complete expansion. However, since the behavior of the matrix elements for large values of α and β is quantitatively very different in the two procedures, one may expect to find significant differences between the two methods in numerical applications.

Thus it is also instructive to compare the limiting behavior of I^{MC} and I^{MR} for large values of α and β. From the asymptotic behavior of $F_0(z)$,

$$F_0(z)\tfrac{1}{2}(\pi/z)^{1/2}-e^{-z}/2z\,, \tag{14}$$

we see that the matrix elements will grow exponentially large if the real part of the argument of F_0 is negative. Examination of Eq. (13) shows that I^{MR} remains well behaved, independent of λ and $\vec{A}$, provided $|\phi|<45°$. For certain choices of λ and $\vec{A}$, however, the real part of the argument of F_0 in Eq. (12) can become negative for any value of ϕ not a multiple of 2π. For example, if the basis functions are centered at the nucleus ($\vec{A}=\vec{R}$), then the real part of the argument of F_0 in the expression for I^{MC} is

$$(\alpha+\beta)R^2(\cos 2\phi/\lambda^2-\cos\phi/\lambda+1)\,,$$

which is negative when

$$\cos\phi-\sin\phi<\lambda<\cos\phi+\sin\phi \tag{15}$$

Thus when ϕ is not zero or an integer multiple of 2π, there is a range of λ for which I^{MC} increases exponentially with increasing α or β, as Moiseyev and Corcoran[4] point out in their footnote 12. This aspect of the Moiseyev-Corcoran procedure means that numerical instabilities can be encountered unless the basis set parameters are carefully chosen.

We saw, in the discussion following Eq. (13) above, that the McCurdy-Rescigno[3] method differs from the Moiseyev-Corcoran[4] procedure in that the basis functions are moved to centers scaled according to $\theta^{-1}\vec{A}$. This is an essential difference because the cusps in the complex wave functions are moved to complex centers in these calculations. We can see how the complex cusps arise in two ways. First, if we regard Eqs. (12) and (13) as having been derived from the integral in Eq. (11) following the substitution $(\vec{r}-\vec{R})^2\rightarrow(\theta\vec{r}-\vec{R})^2$, it is apparent that the integrand is singular at $\theta^{-1}\vec{R}$, and one might expect that the wave functions would correspondingly obey cusp conditions at $\theta^{-1}\vec{R}$. However, since we perform the analytic continuation of Hamiltonian matrix elements using analytic formulas for the integrals, it can be somewhat misleading to argue too literally from the forms of the integrands. After all, we argued in Sec. II that the above scaling transformation leads to a circle of branch points in the nuclear attraction terms of the Hamiltonian. A better way to deduce the location of the cusps in these calculations is to use McCurdy's[6] result that if we find the coefficients d_β by solving the secular equation involving the analytically continued matrix $H_{\alpha,\beta}(\theta)$ of the Moiseyev-Corcoran approach, we form an approximation to the eigenfunctions, ψ_ϕ, of Simon's[5] exterior scaled Hamiltonian of the form

$$\psi_0(\vec{r})\simeq\sum_{\beta=1}^{N}d_\beta\chi_\beta(c(r)\hat{r})\,, \tag{16}$$

where $\chi_\beta(\vec{r})$ is a real Gaussian basis function of the form given in Eq. (10). If, for example, the state in question is a bound state, the exact eigenfunction of the exterior scaled Hamiltonian can be found from the exact bound-state eigenfunction $\psi^{\mathrm{bound}}(\vec{r})$ of the unscaled Hamiltonian by simply evaluating it at $\vec{r}=R(r)\hat{r}$, where $R(r)$ is the exterior scaling contour given in Eq. (3). Thus we have

$$\psi^{\mathrm{bound}}(R(r)\hat{r})\simeq\sum_{\beta=1}^{N}d_\beta\chi_\beta(c(r)\hat{r})\,, \tag{17}$$

and by a simple change of variable in this equation [recall $\theta c(r)=R(r)$] we obtain

$$\psi^{\mathrm{bound}}(\theta\vec{r})\simeq\sum_{\beta=1}^{N}d_\beta\chi_\beta(\vec{r})\,,$$

for the wave function we are expanding in real Gaussian basis functions, $\chi_\beta(\vec{r})$, where $\psi^{\mathrm{bound}}(\theta\vec{r})$ is a bound-state eigenfunction of the real Born-Oppenheimer Hamiltonian evaluated at the complex coordinate $\theta\vec{r}$. Now clearly if $\psi^{\mathrm{bound}}(\vec{r})$ has a cusp at $\vec{r}=\vec{R}$, $\psi^{\mathrm{bound}}(\theta\vec{r})$ has a cusp at $\vec{r}=\theta^{-1}\vec{R}$. Recalling that the McCurdy-Rescigno[3] procedure can be derived from the Moiseyev-Corcoran[4] prescription by translating the basis functions to complex centers $\theta^{-1}\vec{A}$, we see immediately that the McCurdy-Rescigno method allows the complex cusps in the molecular wave functions to be approximated by Gaussians of large exponents on the cusp centers, while the Moiseyev-Corcoran method effectively centers basis functions elsewhere. For this reason we expect the McCurdy-Rescigno procedure to have better convergence properties, and the calculations presented in the following section bear out this expectation. We will defer further discussion comparing the two techniques until Sec. IV.

III. NUMERICAL EXAMPLES

In this section we present the results of photoionization calculations using the approximation to $I(\omega)$ in Eq. (8), with the matrix $\underline{(E_0+\omega-H)_\theta}$ obtained using both the McCurdy-Rescigno[3] and Moiseyev-Corcoran[4] procedures for analytically continuing the matrix elements $H_{\alpha,\beta}(\theta)$. We have chosen to compute the component of the photoionization cross section of H_2^+ for polarization parallel to the molecule (the $1s\sigma_g \rightarrow k\sigma_u$ transition). This particular example presents a rather challenging test for basis-set calculations. The cross section is very small and sensitive to higher angular momentum components of the basis set, and it therefore offers a good measure of the utility of the methods we have employed. Also, because it is a one-electron system, H_2^+ affords a simple example of the problems arising specifically from the form of the molecular nuclear attraction potential and not from the many-electron aspects of the molecular problem which are irrelevant to the discussion here.

To facilitate our comparisons, we have used large basis sets both to calculate the $1s\sigma_g$ ground-state eigenfunction and to represent the matrix $\underline{(E_0+\omega-H)_\theta}$ for the σ_u continuum. In this way, we are able to use the same basis sets for both methods while avoiding the criticism that the basis set was optimum for one method but not for the other. For the ground state, we used a Gaussian basis consisting of the Huzinaga[9] $10s/6p_z$ Gaussian basis for hydrogen on each proton with exponents scaled by 3.0; four d_{z^2} functions on each hydrogen with exponents decreasing from 15.0 in a geometric series of ratio 3.0; twelve s functions at the center of the molecule with exponents decreasing from 14.4 in a geometric series of ratio 3.0; and six d_{z^2} functions at the center molecule with exponents decreasing from 10.0 with a ratio of 3.0. Of the 41 uncontracted functions of σ_g symmetry that can be formed from these functions, 39 orthogonal σ_g basis functions were constructed to avoid linear dependence problems. For the excited-state symmetry(σ_u), we used a basis consisting of Huzinaga's[9] $10s$ hydrogenic basis on each proton with exponents scaled by 3.0; nine p_z functions on each proton, eight of which had exponents decreasing from 3.6 in a geometric series of ratio 1.7 and one with exponent 10.0; and five d_{z^2} functions on each proton with exponents decreasing from 15.0 in a geometric series of ratio 3.0. From this basis 24 uncontracted functions of σ_u symmetry can be formed and 24 orthogonal functions were constructed from these.

We hasten to remark that adequate results (±5%) can be obtained with far smaller basis sets with the more stable of the methods we tried and that these extravagantly large sets of functions were used only to facilitate the comparison of alternative computational procedures using the same basis sets.

After choosing the basis-set exponents in these calculations, one may optimize the scaling parameter θ in a given basis set because the results are formally independent of θ when converged. The usual procedure[7] in atomic calculations is to fix the magnitude of θ at unity and vary the argument to find the region of greatest stability. We did that using the McCurdy-Rescigno prescription for computing $H_{\alpha,\beta}(\theta)$, making no attempt to optimize the magnitude of θ. Figure 1 shows a superposition of five plots of the photoionization cross sections obtained by setting $\theta = \exp(i\pi\phi/180.0)$ and varying ϕ in 2.5° increments over a 10° interval centered approximately at the most stable point in ϕ. The results are stable within a few percent and agree essentially exactly with the exact values of Bates and Öpik.[10]

We repeated this calculation with the procedure of Moiseyev and Corcoran.[4] However, no recognizable region of stability could be found with $|\theta| = 1$, and we therefore varied $|\theta|$ to find a more optimum value. It is not surprising that this was necessary considering the behavior of nuclear attraction integrals with large exponents which Moiseyev and Corcoran[4] point out and which we discussed earlier. We find the most favorable

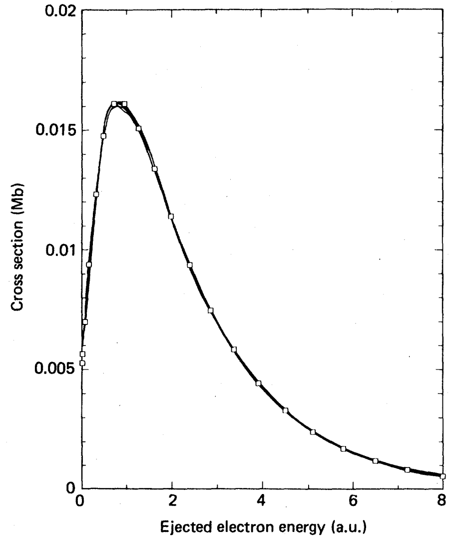

FIG. 1. Superposition of results for the parallel component of the photoionization cross section of H_2^+ computed using the method of Ref. 3 to analytically continue the Hamiltonian matrix elements. The superimposed curves are for ϕ varying over the most stable region (15° to 25°) in 2.5° increments.

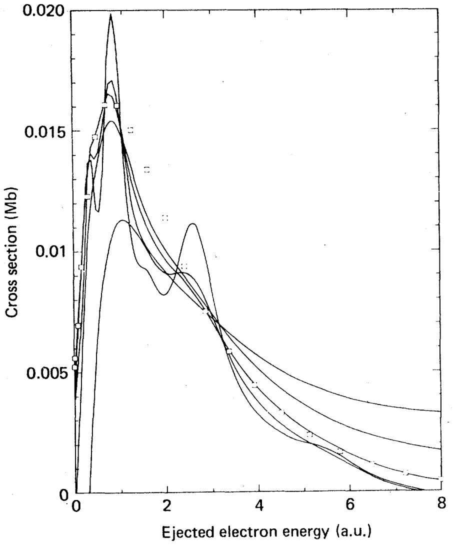

FIG. 2. As in Fig. 1, but using the method of Ref. 4 to analytically continue the Hamiltonian matrix elements. The magnitude of the scaling parameter is 0.6 and ϕ varies from 5° to 15° in 2.5° increments.

value of $|\theta|$ to be approximately 0.6, with little sensitivity for values varying between 0.5 and 0.8. Figure 2 shows a superposition of five plots for the photoionization cross sections obtained with $\theta = 0.6\exp(i\pi\phi/180.0)$ for values of ϕ in 2.5° increments over a 10° interval, again approximately centered in the region of greatest stability. Comparison of Figs. 1 and 2 shows that the Moiseyev-Corcoran[4] technique is substantially less stable in this application than that of McCurdy and Rescigno.[3] Although it is possible that the results in Fig. 2 could be improved slightly by further optimization of $|\theta|$, we conclude that no substantial improvement can be affected and that this calculation remains dramatically less stable to variations in θ than that of Fig. 1.

Another indication of the relative stability of the two methods is given by the extent to which the ground-state energy appears as a real eigenvalue of $H_{\alpha,\beta}(\theta)$ in the orthogonal basis. Picking the value of ϕ at which each calculation gives the best results for the cross section, we find that at $\phi = 20°$ the McCurdy-Rescigno version of the calculation gives $E_0^{\mathrm{MR}} = -1.102\,637 + i1.36\times 10^{-7}$ a.u., and that at $\phi = 10°$ (but at different $|\theta|$ as noted above) the Moiseyev-Corcoran version of the calculation gives $E_0^{\mathrm{MC}} = -1.098\,114 + i1.30\times 10^{-3}$ a.u. The exact value is $-1.102\,634$ a.u. The implication of this result is that in a calculation in which resonance energies are computed as eigenvalues of $H_{\alpha,\beta}(\theta)$, and extreme accuracy is therefore required in both the real and imaginary parts of the eigenvalues, the McCurdy and Rescigno procedure will provide more reliable results in a given basis. However, this assertion will have to be verified in a resonance calculation.

IV. DISCUSSION

We have compared two numerical procedures for computing molecular photoionization cross sections in the Born-Oppenheimer approximation using complex basis functions. We have argued that one of the procedures,[4] which is based superficially on the complex scaling transformation used for atomic problems,[1] is likely to converge slowly because it effectively moves the expansion basis off the centers at which cusps occur in the complex molecular eigenfunctions. This supposition was illustrated with calculations of the photoionization cross section of H_2^+.

In comparing the two methods, we have concentrated on the behavior of the matrix elements of the nuclear attraction terms, since their nonanalytic behavior has hindered the application of complex scaling techniques to molecular problems. Moiseyev and Corcoran have also emphasized that the computation of two-electron matrix elements, which is the most time-consuming part of integral evaluation, is simpler with their procedure since the integrals are simply scaled by constants and need not be recomputed when the scale parameters are changed.[4] It is noteworthy, however, that several applications of complex scaling techniques to atomic problems involving more than two electrons have shown that accurate results can only be achieved when the orbitals referring to tightly bound core electrons are left unscaled and the outer valence electron orbitals made complex.[11,12] If such a procedure were also adopted in molecular applications, the two-electron integrals would no longer scale simply and the computational details involved in implementing the two methods would be quite similar. Application of these techniques to realistic molecular systems is currently underway.

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