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Complex-coordinate calculation of matrix elements of the resolvent of the Born-Oppenheimer Hamiltonian

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A procedure is outlined for using complex scaling to compute matrix elements of the resolvent of the Born-Oppenheimer Hamiltonian for a molecule with respect to square integrable functions. The method is superficially identical to that used previously for computing atomic photoionization cross sections—even though the molecular Born-Oppenheimer Hamiltonian is ill behaved under the scaling transformation appropriate to the atomic problem. The author gives a heuristic derivation of the method, relating it to Simon's theory of exterior complex scaling, which treats the molecular Born-Oppenheimer problem correctly. Numerical results are presented for H_2^+ photoionization cross sections for which exact results are available for comparison.

I. INTRODUCTION

The successful application of the method of complex scaling (rotated coordinates)[1] to resonance problems in electron-atom scattering has stimulated considerable interest in the development of generalizations of the method which are applicable to other continuum processes. The theory of complex scaling, as it was originally developed[1] and applied to atomic problems, is limited to Hamiltonians which are dilatation analytic. The now familiar $r \to re^{i\phi}$ transformation of all electronic radial coordinates is a direct application of the theory for dilatation-analytic potentials.

Although this limitation seemed quite formidable at first, we are gradually discovering that extending the original ideas to nondilatation-analytic problems can be quite straightforward. For example, progress has been made in the treatment of resonances in the Stark problem[2] where *translational* analyticity can be exploited. Also, the first steps have been taken, both theoretically and computationally, in the generalization of complex scaling to the treatment of molecular resonances within the Born-Oppenheimer framework.[3-5] However, this problem is far from being well understood.

As we will discuss in Sec. II, it is the Born-Oppenheimer approximation which is responsible for the absence of dilatation analyticity in the molecular problem. The complete Hamiltonian of the system of electrons and nuclei is dilatation analytic. However, it is highly impractical to abandon the Born-Oppenheimer approximation in electron-molecule scattering calculations. Also, as McCurdy and Rescigno[4] pointed out, there are electronic resonance states whose complex resonance eigenvalues yield dissociative potential surfaces in the Born-Oppenheimer picture. Since they correspond to continuum states for nuclear motion, these states would not appear as isolated poles of the resolvent of the complete molecular Hamiltonian, although they do correspond to features of the cross section. The simple description of these states is another reason for retaining the Born-Oppenheimer picture.

The only mathematically rigorous discussion of complex coordinates in the Born-Oppenheimer approximation to the molecular problem which has been given to date is the work of Simon,[3] who has suggested a method he calls "exterior complex scaling." At first glance Simon's proposal appears extremely impractical for numerical calculations. On the other hand, McCurdy and Rescigno,[4] as well as Moiseyev and Corcoran,[5] have described numerical procedures for molecular resonances which are within the realm of practicality but have been given only scant theoretical justification.

The purpose of this paper is to demonstrate that the numerical procedure of Ref. 5 can be extended to the computation of resolvent matrix elements, and to provide an argument for why this is possible. In particular, we compute molecular photoionization cross sections using this approach. The prescription we use is superficially identical to that used in the case of a dilatation-analytic Hamiltonian under the scaling $r \to re^{\theta}$, although, as will become apparent from the discussion in the following sections, it is certainly *not* the case that our procedure makes the ordinary complex-scaling transformation on the Born-Oppenheimer Hamiltonian.

We offer a possible way to view the connection between the numerical procedure of Ref. 5 and Simon's rigorous theory of exterior complex scaling in the discussion of Sec. IV, and we provide a heuristic derivation of our successful numerical procedure for calculating resolvent matrix elements. A key to understanding how the numerical procedure we use accomplishes the analytic continuation of the Born-Oppenheimer Hamiltonian is to note that an important feature of the molecular problem (and in fact of the atomic problem as well) is that the Hamiltonian as a function of electronic coordinates may be continued onto a family of complex contours, all of which generate continuations of the Hamiltonian with the same spectrum. This fact is particularly apparent in Simon's exterior-scaling theory[3] in which a set of contours yielding the same spectrum is given by varying his parameter R_0. By performing contour distortions of the integrations in the matrix elements of the Hamiltonian, it can be shown that the analytic continuation we use is equivalent to computing matrix elements of the Hamiltonian of the exterior-scaling theory with respect to complex basis functions. Although this interpretation is not unique, it provides some understanding of why the numerical procedure we use works, particularly in the case of computing resolvent matrix elements.

In Sec. II we briefly outline Simon's exterior-complex-scaling procedure, and in Sec. III we describe the numerical procedures we will use. In Sec. IV we present a discussion of the relationship between the numerical procedures and exterior complex scaling and outline our procedure for computing resolvent matrix elements. Section V presents some numerical results, and concluding remarks are made in Sec. VI.

II. EXTERIOR COMPLEX SCALING

First of all let us establish the need in the Born-Oppenheimer problem for something other than the simple scaling transformation, $r \rightarrow re^{\theta}$ for all electronic coordinates, with θ complex. In the Born-Oppenheimer Hamiltonian (atomic units),

$$H = -\tfrac{1}{2}\sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N}\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} + \tfrac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}\,, \tag{1}$$

the only term which causes problems under the transformation $r \rightarrow re^{\theta}$ is the nuclear-attraction potential. Consider one of the nuclear-attraction terms in which we perform the scaling transformation with $\theta = i\phi$, ϕ real. Using the correct expression for the vector distance, we have

$$1/|\vec{r}e^{i\phi} - \vec{R}| \equiv 1/[(\vec{r}e^{i\phi} - \vec{R})^2]^{1/2}\,. \tag{2}$$

As Simon[3] points out, for real $\vec{r}$ this expression has a circle of square-root branch points with r satisfying

$$|\vec{r}| = |\vec{R}|\,, \quad \hat{r}\cdot\hat{R} = \cos\phi\,. \tag{3}$$

Thus the potential due to the nuclei becomes a pathological function of real $\vec{r}$ with continuous sets of branch points. Clearly this procedure does not define a useful analytic continuation of the Born-Oppenheimer Hamiltonian.

So in order to compute resonance positions, etc., with this technique, we must find a generalization of the complex-scaling transformation under which the Hamiltonian is analytic and which provides us with an operator whose (complex) spectrum is similar to that of the atomic Hamiltonian under $r \rightarrow re^{\theta}$.

Simon's[3] solution to this problem is to scale the magnitudes of all electronic coordinates according to $r \rightarrow R(r)$, where

$$R(r) = \begin{cases} r, & 0 < r \leq R_0 \\ R_0 + e^{\theta}(r - R_0), & R_0 \leq r \end{cases} \tag{4}$$

(see Fig. 1), and R_0 is sufficiently large that the potential due to the nuclei is analytic for $r > R_0$. This transformation avoids all the branch points of the nuclear-attraction terms. In order that this transformation remain unitary, it is necessary to introduce a Jacobian factor

$$J(r) = \left(\frac{dR(r)}{dr}\right)^{1/2} \frac{R(r)}{r} \tag{5}$$

in the operator $U_{R_0}(\theta)$, which performs the transformation so that for one electron we have that $U_{R_0}(\theta)$ operates on a function of r to give (with $|\hat{r}| = 1$)

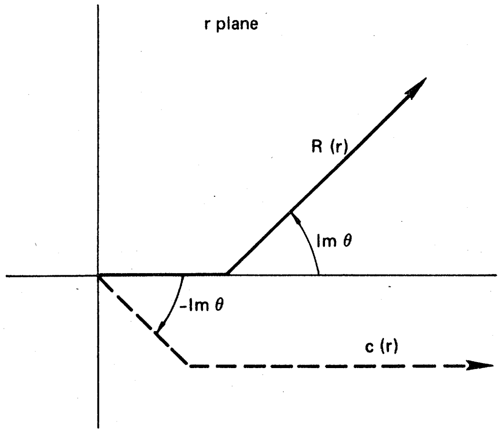

FIG. 1. Contours $R(r)$ (solid) and $c(r)$ (broken). $R(r)$ is the contour for the exterior-scaling transformation, and $c(r)$ is used in the integrations in Sec. IV.

$$(U_{R_0}(\theta)\Psi)(\vec{r}) = J(r)\Psi(R(r)\hat{r}) \tag{6}$$

with an obvious generalization to N electrons. The exterior-scaling Hamiltonian $H_{R_0}(\theta)$ is defined by

$$H_{R_0}(\theta) = U_{R_0}(\theta) H U_{R_0}^{-1}(\theta)$$

and is given by

$$H_{R_0}(\theta) = \sum_{i=1}^{N} h_{R_0}^{i}(\theta) - \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|R(r_i)\hat{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|R(r_i)\hat{r}_i - R(r_j)\hat{r}_j|}\,, \tag{7}$$

where

$$h_{R_0}^{i}(\theta) = \begin{cases} -\frac{1}{2}\nabla_i^2\,, & 0 < r_i \leq R_0 \\ -\frac{1}{2}e^{-2\theta}\nabla_i^2\,, & R_0 < r_i\,. \end{cases} \tag{8}$$

Since for larger r_i the exterior-scaling transformation is the same as ordinary complex scaling, one might expect that $H_{R_0}(\theta)$ would have the same spectrum as the more familiar rotated-coordinate Hamiltonian. In fact, Simon[3] has been able to prove that this is the case. The spectrum of $H_{R_0}(\theta)$ is made up of isolated bound-state and resonance eigenvalues together with rays of continuous eigenvalues rotated by $2\,\mathrm{Im}(\theta)$.

It appears that it would be extremely difficult to form matrix elements of $H_{R_0}(\theta)$ with respect to the ordinary Gaussian basis functions used in calculations of bound-state molecular wave functions. So although exterior complex scaling solves the formal problems in the generalization of complex scaling to the Born-Oppenheimer Hamiltonian, it does not have the appealing computational simplicity of the complex-coordinate approach for atoms. Nevertheless, we will assert in Sec. IV that it appears that recent numerical calculations have implemented this theory implicitly.

III. RECENTLY PROPOSED NUMERICAL PROCEDURES

We will discuss the method used by Moiseyev and Corcoran[5] in their calculations on H_2 and H_2^-. We specialize to the case of a one-electron molecule for notational simplicity. The generalization to many electrons is obvious.

Moiseyev and Corcoran observed that no matter what pathologies the Born-Oppenheimer Hamiltonian exhibits under the usual scaling transformation $\vec{r} \to \vec{r}e^{\theta}$, the Gaussian matrix elements of the Born-Oppenheimer Hamiltonian, all of which can be evaluated analytically, are entire functions of θ. So they simply used the analytic formulas for the matrix elements to evaluate the analytic continuation of the matrix representation of the Hamiltonian to complex values of θ.

In other words, if we define the matrix $\mathcal{H}_{\alpha\beta}(\theta)$ for *real* θ by the matrix elements with respect to basis functions χ_α of the Born-Oppenheimer Hamiltonian $H_{\mathrm{BO}}^{(\theta)}$ in which the electronic coordinates are scaled according to $\vec{r}e^{\theta}$,

$$\mathcal{H}_{\alpha,\beta}(\theta) = \int \chi_\alpha(\vec{r}) H(\theta)_{\mathrm{BO}} \chi_\beta(\vec{r})\, d^3r \quad (\text{real } \theta)\,. \tag{9}$$

Moiseyev and Corcoran construct the analytic continuation of the *matrix elements* $\mathcal{H}_{\alpha,\beta}(\theta)$ to complex θ. From our discussion in Sec. II, it is clear that this is *not* the same as forming matrix elements of the operator $H_{\mathrm{BO}}(\theta)$ for complex values of θ. However, when the resulting complex matrix was diagonalized to produce an approximate spectrum, Moiseyev and Corcoran[5] found that the bounds states and resonance eigenvalues as well as the approximate continuum eigenvalues of this matrix behave in the same way as the corresponding eigenvalues in the atomic problem under the usual complex-coordinate transformation. This procedure has in fact constructed some analytic continuation of the Born-Oppenheimer Hamiltonian which appears, within the basis-set approximation, to display the same spectrum as Simon's exterior-scaling Hamiltonian.

In this approach the two-electron and kinetic-energy matrix elements offer no problem; they are simply scaled by constants, but it is instructive to examine what happens in the matrix elements of the nuclear-attraction potential. A matrix element between s-type Gaussian functions of one term of the nuclear potential is given by

$$I = \int e^{-a(\vec{r}-\vec{A})^2} \frac{1}{[(\vec{r}-\vec{R})^2]^{1/2}} e^{-b(\vec{r}-\vec{B})^2}\, d^3r = \frac{2\pi}{a+b} \times F_0((a+b)(\vec{R}-\vec{P})^2) \exp\left(-\frac{ab}{a+b}(\vec{A}-\vec{B})^2\right)\,, \tag{10}$$

where

$$\vec{P} = (a\vec{A} + b\vec{B})/(a+b) \tag{11}$$

and $F_0(z)$ is the entire function of z given by

$$F_0(z) = \tfrac{1}{2}(\pi/z)^{1/2}\,\mathrm{erf}(z)\,. \tag{12}$$

If we define $I(\theta)$ as the integral in Eq. (10) with $(\vec{r}-\vec{R})^2$ replaced by $(\vec{r}e^{\theta}-\vec{R})^2$, then for real θ we find $I(\theta)$ is simply given by (factor $e^{-\theta}$ out of the integrand)

$$I(\theta) = \frac{2\pi e^{-\theta}}{a+b} F_0((a+b)(\vec{R}e^{-\theta} - \vec{P})^2) \times \exp\left(-\frac{ab}{a+b}(\vec{A}-\vec{B})^2\right)\,. \tag{13}$$

Moiseyev and Corcoran constructed the analytic continuation of the nuclear-attraction-potential matrix elements by evaluating Eq. (13) at complex θ.

Although there are choices of θ which lead to large values of $I(\theta)$ for some physically reasonable a and b, and result in numerical instabilities in the matrix manipulations, Eq. (13) is entirely well behaved in θ. In Sec. IV we will ask how we would construct $I(\theta)$ for complex values of θ if the analytic formula were not available. This question will lead to an apparent connection with exterior complex scaling.

IV. RELATIONSHIP OF NUMERICAL PROCEDURES TO EXTERIOR COMPLEX SCALING AND THE COMPUTATION OF RESOLVENT MATRIX ELEMENTS

The analytic continuation of the matrix elements which is performed using analytic formulas in the numerical calculations of Sec. III can also be performed by contour distortions in the integrals. Viewing the problem in this way allows us to see that the matrix elements $\mathcal{H}_{\alpha,\beta}$ of Eq. (9) when evaluated for complex θ can be interpreted as matrix elements of the exterior-scaling Hamiltonian. As noted in the Introduction, this is not a unique interpretation, since there is a wide class of continuations of the Born-Oppenheimer Hamiltonian which have the same spectrum. The value of our point of view is that it allows us to (at least heuristically) derive a procedure for computing resolvent matrix elements.

Again it is only necessary to examine the matrix elements of the nuclear-attraction potential in detail; the kinetic-energy and electron-repulsion terms do not pose any problems. The problem is to find a contour c for the radial integrations such that in each Gaussian integral, we have (for complex θ)

$$I(\theta)=\int d\Omega\int_c dr\, r^2\,\frac{1}{[(\vec{r}e^{\theta}-\vec{C}^2]^{1/2}}\times e^{-b(\vec{r}-\vec{B})^2}, \tag{14}$$

where $I(\theta)$ is given by Eq. (13). We cannot simply perform the integral in Eq. (14) along the real r axis because the argument of the square root $\zeta(\vec{r})$

$$\zeta(\vec{r})=(\vec{r}e^{\theta}-\vec{C})^2, \tag{15}$$

will encircle the branch point for some r when θ is complex. Figure 2 compares the path of $\zeta(\vec{r})$ for $0<r<\infty$ for $\theta=\phi$ with that when $\theta=i\phi$, $\phi>0$ with a particular choice of $\hat{r}$ and $\hat{C}$.

The key to finding the contour, which we will denote by the function $c(r)$ for real r, is to require that

$$\mathrm{Re}\{[c(r)\hat{r}e^{\theta}-\vec{C}]^2\}>0\,.$$

If this is the case, the square root in Eq. (14) will

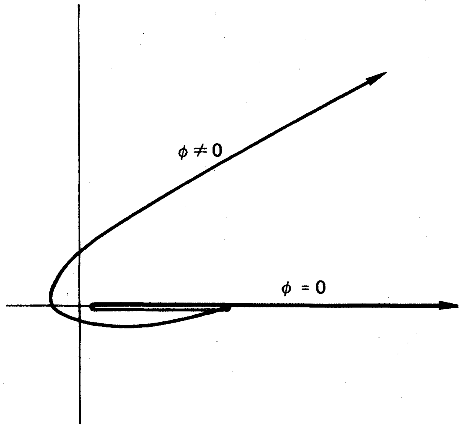

FIG. 2. Function $\zeta(r)$ defined in Eq. (15) for two choices of ϕ. See text.

continuously become the positive square root as $\mathrm{Im}(\theta)\to 0$ for all r. Such a contour is given by $c(r)$ defined by

$$\begin{aligned} c(r)&=re^{-\theta}\,, \quad 0<r\leq R_0\,,\\ c(r)&=R_0e^{-\theta}+(r-R_0)\,, \quad R_0\leq r\,, \end{aligned} \tag{16}$$

where R_0 is defined as for $R(r)$ in Eq. (4). Note that $e^{\theta}c(r)$ is $R(r)$. This choice of $c(r)$ is shown in Fig. 1 as the broken curve. We can perform this contour distortion in the Gaussian matrix elements of the kinetic-energy and electron-repulsion terms as well, where we first set $\vec{r}=\vec{r}e^{\theta}$ for all electronic coordinates in the operators. No nonanalyticity problems arise. And in every case, since $e^{\theta}c(r)=R(r)$, the contour distortion transforms the operators into their exterior-scaling forms.

The end result of this operation is to derive the following identity. We will hereafter specialize to the case of a one-electron molecule for notational simplicity. The electron-repulsion terms pose no special problems, and the generalization to the many-electron case is straightforward.

$$\mathcal{H}_{\alpha,\beta}(\theta)=\int d^3r\,\frac{dc(r)}{dr}\,\frac{c(r)^2}{r^2}\,\chi_{\alpha}(c(r)\hat{r})\times H_{R_0}(\theta)\chi_{\beta}(c(r)\hat{r})\,, \tag{17}$$

where $\mathcal{H}_{\alpha,\beta}(\theta)$ is the analytic continuation to complex θ of the function of real θ given in Eq. (9), and $H_{R_0}(\theta)$ is the exterior-complex-scaling Hamiltonian of Eq. (7) for one electron. Thus, we may interpret $\mathcal{H}_{\alpha,\beta}(\theta)$ in the Moiseyev and Corcoran[5] calculation as a matrix element of the exterior-scaling Hamiltonin with respect to the complex functions $\chi(c(r)\hat{r})$. The Jacobian factor $[dc(r)/dr][c(r)/r]^2$ plays the role of a weighting function and does not affect this interpretation.

One can think of Eq. (17) as having arisen from the solution of

$$(H_{R_0}(\theta) - E)\Psi = 0 \tag{18}$$

by a Galerkin[6] approximation in which Ψ is expanded,

$$\Psi(\vec{r}) = \sum_{\beta} C_\beta \chi_\beta(c(r)r), \tag{19}$$

and in which we form equations for the coefficients C_β by multiplying Eq. (18) by

$$\frac{dc(r)}{dr}\,\frac{c(r)^2}{r^2}\,\chi_\alpha(c(r)r)$$

and integrating over electronic coordinates. This yields the secular equation for C_β and E as the eigenvector and eigenvalue of $\mathcal{H}_{\alpha,\beta}(\theta)$.

We can use this picture to derive an approximation to resolvent matrix elements. Suppose we wish to approximate

$$I = \int d^3r \int d^3r'\, f(\vec{r})G(z,\vec{r},\vec{r}\,')g(\vec{r}\,'), \tag{20}$$

where $G(z,\vec{r},\vec{r}\,')$ is the resolvent of the real Hamiltonian $(z-H)^{-1}$, and $f(r)$ and $g(r)$ are L^2 and analytic in the region required in the contour distortions below. If we distort the integration contours in Eq. (20) onto the contour $R(r)$, we find

$$I = \int d^3r\, J^2(r) \int d^3r'\, f(R(r)\hat{r})G_R(z,\vec{r},\vec{r}\,') \times g(R(r')\hat{r}), \tag{21}$$

where $J(r)$ is the Jacobian defined in Eq. (5) and $G_R(z,\vec{r},\vec{r}\,')$ is the resolvent of the exterior-scaling Hamiltonian, $[z - H_{R_0}(\theta)]^{-1}$, in the coordinate representation. We can approximate the integral $\mathfrak{F}(z,r)$ defined

$$\mathfrak{F}(z,r) = \int d^3r'\, G_R(z,\vec{r},\vec{r}\,')g(R(r')\hat{r}) \tag{22}$$

appearing in Eq. (21) by a Galerkin[6] approximation such as we used to approximate the solutions of Eq. (18). The function $\mathfrak{F}(z,r)$ satisfies the differential equation

$$(z - H_{R_0}(\theta))\mathfrak{F}(z,r) = g(R(r)\hat{r}). \tag{23}$$

By expanding $\mathfrak{F}(z,r)$ in Eq. (23) in terms of the basis functions $\chi_\beta(c(r))$,

$$\mathfrak{F}(z,r) = \sum_{\beta}{}' d_\beta \chi_\beta(c(r)), \tag{24}$$

multiplying the equation by

$$\frac{dc(r)}{dr}\left(\frac{c(r)}{r}\right)^2 \chi_\alpha(c(r)),$$

and integrating over $\vec{r}$, we obtain a matrix equation for the coefficients d_β.

$$\vec{d} = (z-H)_\theta^{-1}\vec{g}. \tag{25}$$

The elements of $\vec{g}$ are defined by [we have used $c(r) = e^{-\theta}R(r)$]

$$g_\alpha = e^{-3\theta} \int d^3r\, J^2(r)\chi_\alpha(c(r)\hat{r})\, g(R(r)\hat{r}) \tag{26}$$

and $(z-H)_\theta^{-1}$ is the inverse of the matrix (depending on θ but not R_0)

$$(z-H)^{(\theta)}_{\alpha,\beta} = \int d^3r\, \frac{dc(r)}{dr}\,\frac{c(r)}{r^2}\,\chi_\alpha(c(r)\hat{r}) \times (z - H_{R_0}(\theta))\chi_\beta(c(r)\hat{r}), \tag{27}$$

which is no more than $\mathcal{H}_{\alpha,\beta}(\theta)$ from the analytic continuation of Eq. (9) plus a constant. Substituting the resulting expression for $\mathfrak{F}(z,r)$ into Eq. (21) yields

$$I \simeq e^{3\theta}\,\vec{f}(z-H)_\theta^{-1}\vec{g}, \tag{28}$$

where the elements of $\vec{f}$ are defined

$$f_\alpha = e^{3\theta} \int d^3r\, J^2(r)\chi_\alpha(c(r)\hat{r})\, f(R(r)\hat{r}). \tag{29}$$

The final step is to make yet another contour distortion, this time in the integrals of Eqs. (26) and (29) onto the contour which undoes the $r \rightarrow c(r)$ distortion [assuming $f(\vec{r})$ and $g(\vec{r})$ are such that we can do this]. *But we do not do so in the matrix elements in Eq.* (27). Then, using $R(r) = e^\theta c(r)$, we have

$$\begin{aligned} f_\alpha &= \int d^3r\, f(\vec{r}e^\theta)\chi_\alpha(\vec{r}), \\ g_\alpha &= \int d^3r\, g(\vec{r}e^\theta)\chi_\alpha(\vec{r}). \end{aligned} \tag{30}$$

With this equation we have arrived at our prescription for calculating resolvent matrix elements with respect to well-behaved functions f and g: (i) Form the analytic continuation of $\mathcal{H}_{\alpha,\beta}(\theta)$ in Eq. (9) to complex θ and use that to construct the matrix $(z-H)_\theta^{-1}$ in Eq. (28). (ii) Construct the integrals $\vec{f}$ and $\vec{g}$ in Eq. (30), which have the form of integrals arising in ordinary complex scaling. (iii) Form the matrix product in Eq. (28).

The final result is that if one can compute the analytic continuation of $\mathcal{H}_{\alpha,\beta}(\theta)$, the computation of resolvent matrix elements proceeds thereafter as though one were simply performing the complex-scaling transformation. The procedure outlined above is essentially identical to that used in atomic photoionization calculations,[7] as is apparent from our molecular photoionization calculations in Sec. V.

V. MOLECULAR PHOTOIONIZATION CALCULATIONS

The photoionization cross section can in general be computed from the imaginary part of the frequency-dependent polarizability.[8] In atomic units we have

$$\sigma(\omega)=(4\pi\omega/c)\,\mathrm{Im}[\alpha^{-}(\omega)]\,, \tag{31}$$

with the frequency-dependent polarizability $\alpha^{-}(\omega)$ defined by

$$\alpha^{-}(\omega)=\left\langle\Psi_0\left|\mu\frac{1}{H-E_0-\omega-i\epsilon}\mu\right|\Psi_0\right\rangle\,, \tag{32}$$

where Ψ_0 is the wave function of the atom or molecule in its initial state, and μ is the dipole operator, $\sum_i\hat{e}\cdot\vec{r}_i$, for polarization $\hat{e}$.

The matrix element in Eq. (32) can be approximated using the procedure of Sec. IV. In this way we have computed the photoionization cross section of H_2^+ for transitions into the π_u continuum from the ground state ($1s\sigma_g$) and the first excited state of σ_g symmetry ($2s\sigma_g$). In the notation of Eq. (20), $f(r)$ and $g(r)$ are both $\mu\Psi_0$; so in order to compute the integrals f_α and g_α of Eq. (30), we require $\Psi_0(\vec{r}e^\theta)$. We can, however, obtain an alternate expression in which we use the discrete-basis approximation to Ψ_0 in Eq. (19) to compute these integrals. Using Eq. (19), the assumption that the bound-state eigenfunction of $H_{R_0}(\theta)$ corresponding to Ψ_0 is just $\Psi_0(R(r)\hat{r})$, and using the convenient normalization

$$\int\Psi_0(R(r)\hat{r})\Psi_0(R(r)\hat{r})\frac{dc(r)}{dr}\,\frac{c(r)^2}{r^2}\,d^3r=1\,.$$

We find, for basis functions $\chi_\beta(\vec{r})$,

$$f_\alpha=e^{-3\theta}\sum_\beta C_\beta\int\chi_\beta(\vec{r})\mu(\vec{r}e^\theta)\chi_\alpha(\vec{r}) \tag{33}$$

and the same expression for g_α. Since e^θ can be factored out of $\mu(\vec{r}e^\theta)$, we only have to compute real transition-moment matrix elements between the basis functions $\chi_\alpha(\vec{r})$. Thus we first diagonalize $\mathcal{H}_{\alpha,\beta}(\theta)$ for the initial-state symmetry to compute the coefficients C_β in Eq. (33), and then construct $\mathcal{H}_{\alpha\beta}(\theta)$ for the continuum symmetry (π_u in our examples). Using Eq. (28) and constructing the matrix inverse $(z-H)_\theta^{-1}$, with $z=E_0+\omega$, by diagonalizing $\mathcal{H}_{\alpha,\beta}(\theta)$ for the excited-state symmetry, we complete our approximation for $\alpha^{-}(\omega)$. Thus we essentially follow the same numerical procedure used to compute photoionization cross sections previously[7] used for atoms.

Some numerical results of this calculation are shown in Figs. 3 and 4. We found it necessary to use a large basis to describe the state Ψ_0 for both the $1s\sigma_g$ and $2s\sigma_g$ cross section. We used the Huzinaga[9] 10s and 6p Gaussian basis sets with exponents scaled by 3 centered on each proton and augmented this basis with 12s-type Gaussians at the center of the molecule as well as four additional (three p and one s) functions of large exponent on each proton. From this set we can form a total of 32 basis functions of σ_g symmetry. The results shown in Figs. 3 and 4 were computed with a π_u basis of only 9p-type Gaussians on each proton. For both calculations the value of e^θ was $0.8\exp(0.244i)$. The results are com-

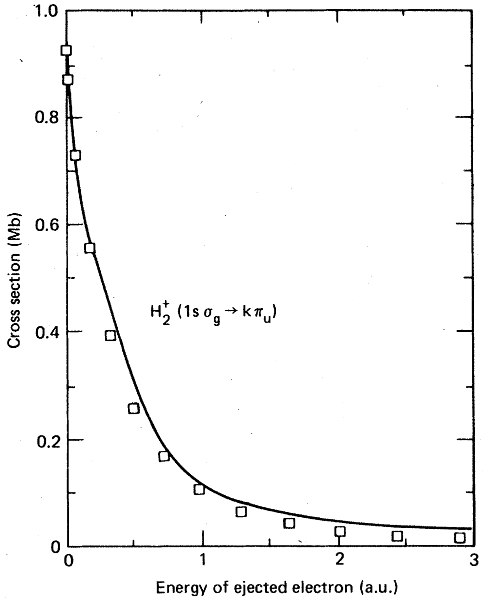

FIG. 3. Calculated photoionization cross section of the $1s\sigma_g$ state of H_2^+ for transitions to the π_u continuum (solid) and the exact results of Ref. 10.

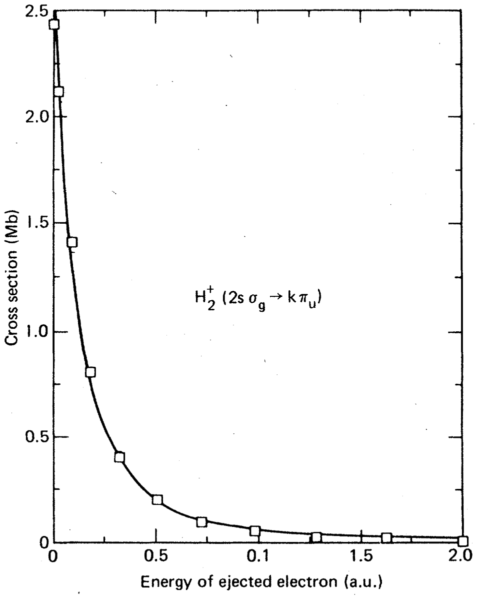

FIG. 4. Calculated photoionization cross section of the $2s\sigma_g$ state of H_2^+ for transitions to the π_u continuum (solid) and the exact results of Ref. 10.

pared with the exact results of Bates and Öpik[10] and show remarkably good agreement.

We observed that for this basis the cross section is stable (within 10%) with respect to varying the imaginary part of θ for only a range of about 7° in $\arg(e^{\theta})$. This is in contrast with the much more stable behavior of atomic calculations by the same method.[7] In principle a converged result would be independent of θ. We have not made an exhaustive study of the convergence of the method as the number of basis functions is increased. However, we have found that for somewhat larger π_u basis sets (15 functions on each center), the region of stability of the cross section is not dramatically increased.

VI. CONCLUSION

We have demonstrated with a numerical calculation that matrix elements of the resolvent of the Born-Oppenheimer Hamiltonian can be computed using the complex-coordinate technique. The method superficially appears to be simple complex scaling which we know to be inapplicable in the case of the Born-Oppenheimer Hamiltonian for a molecule. We have offered a heuristic derivation of the method by showing how to interpret it in terms of Simon's[3] exterior complex scaling. Although this is by no means the only way to view the analytic continuation of the Hamiltonian matrix elements we use, it at least gives some insight into the nature of that analytic continuation.

There appears to be a need for some additional refinement or modification of the method before it shows the same numerical stability as shown in atomic applications.[7] In a later paper we will investigate some alternatives, in particular the McCurdy and Rescigno procedure.[4] It can be shown that the latter procedure for resonance calculations is the same as that of Ref. 5 but with Gaussian basis function centered, not on the nuclear centers $\vec{R}_{\alpha}$, but instead on complex centers, $e^{-\theta}\vec{R}_{\alpha}$. Thus the method of McCurdy and Rescigno[4] can be extended to the computation of molecular photoionization cross sections in exactly the same way as the method of Moiseyev and Corcoran[5] was extended in the present paper. Preliminary indications are that some light can be shed on the lack of numerical stability we observed in Sec. V by asking what becomes of the cusps in the wave functions at nuclear centers in a molecular complex-coordinate calculation. We will explore that question in a future publication.

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