On the direct complex scaling of matrix elements expressed in a discrete variable representation: Application to molecular resonances

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We present an extension of a method initially proposed by Moiseyev and Corcoran [Phys. Rev. A **20**, 814 (1978)] to a *direct* continuation of the matrix elements of a real Hamiltonian operator expressed in a contracted, discrete variable representation type basis set. It is based on the identity which relates the matrix elements of a complex scaled potential between real basis set functions to those of the *unscaled* potential between backward scaled basis functions. The method is first applied to the study of the resonances of a one dimensional model by means of complex scaling. It is shown that the resulting matrix elements of the scaled potential are no longer diagonal in the DVR. This paradox is discussed and shown to be of no practical consequence in the formulation. The scheme is then extended to the direct complex scaling of a two dimensional Hamiltonian operator expressed in a contracted basis set built through the successive adiabatic reduction method of Bačić and Light. Results show that, due to the use of a numerical continuation, slightly larger grids have to be used as compared to the case of an analytic continuation where the potential is available. © *1996 American Institute of Physics.* [S0021-9606(96)01616-8]

I. INTRODUCTION

The problem of analytic continuation of a potential energy function $V(\mathbf{q})$ is of central importance when using the method of complex scaling for the calculation of resonances.[1–4] This requirement has mainly limited its use so far to analytic functions such as Coulomb, pairwise or LEPS potentials. In order to apply the method with arbitrary molecular potentials, such as those coming out of an *ab initio* calculation, one needs a systematic procedure. Different methods have been proposed, essentially based on the continuation of the potential matrix elements evaluated in some convenient basis set.[5,6] Amongst these latter methods, the identity

$$\overline{V}_{ij}=\int dx\,\varphi_i(x)V(xe^{i\theta})\varphi_j(x)$$
$$=e^{-i\theta}\int dx\,\varphi_i(xe^{-i\theta})V(x)\varphi_j(xe^{-i\theta}), \tag{1}$$

was first applied by Moiseyev and Corcoran[7] to the study of molecular resonances of H_2 and H_2^-. This equation relates the matrix elements $\overline{V}_{ij}$ of the complex scaled potential $\overline{V}(x)\equiv V(xe^{i\theta})$ between *unscaled* basis functions $\{\varphi_i\}$ to those of the unscaled potential potential $V(x)$ between backward *scaled* basis functions $[\widetilde{\varphi}_i(x)\equiv\varphi_i(xe^{-i\theta})]$. It is based on the assumption that an exact molecular potential is dilation analytic. In the following, we will use a bar to denote forward scaling, such as $\overline{V(x)}\equiv V(xe^{i\theta})$, and a tilde for the backward scaling, as in $\widetilde{\varphi}_i(x)\equiv\varphi_i(xe^{-i\theta})$.

Equation (1) is of central importance as it shifts the scaling from the potential to the basis functions $\{\varphi_i\}$ which are known *analytically*. This procedure was later successfully applied by Datta and Chu[8] to the rotational predissociation of Ar–N_2. In the same line, Ryabov and Moiseyev[9] recently proposed a method aimed at directly providing the complex scaled matrix elements of a real potential $V(x)$ determined by its values on a grid $\{x_p\}$. This procedure was successfully applied to the determination of the predissociation resonances of the three dimensional HCO and DCO radicals. Using a discrete variable representation[10–12] (DVR) for the Jacobi angle α, they first computed the matrix elements of the complex scaled potential $V(Re^{i\theta},r,\alpha)$ at fixed values α_γ. (R corresponds here to the H–CO dissociation coordinate.) By diagonalization of the resulting complex scaled Hamiltonian $H(Re^{i\theta},r,\alpha_\gamma)$, they were able to obtain *prediagonalized* complex scaled ray-eigenstates $\{|\overline{\Phi}_m(\alpha_\gamma)\rangle\}$ in order to reduce the size of the overall basis set $\{|\overline{\Phi}_m(\alpha_\gamma)\rangle|\alpha_\gamma\rangle\}$.

In this paper we adopt a different point of view, and show how one can directly obtain the complex scaled matrix elements, starting only from *unscaled* ones,

$$\langle R_p|\langle\Phi_m(R_p)|H|\Phi_{m'}(R_{p'})\rangle|R_{p'}\rangle \tag{2}$$
$$\Downarrow$$
$$\langle R_p|\langle\Phi_m(R_p)|\overline{H}|\Phi_{m'}(R_{p'})\rangle|R_{p'}\rangle.$$

The main difference with respect to Ryabov and Moiseyev's approach stems from the fact that ours is equivalent to a numerical continuation of multidimensional elements as shown by Eq. (2). Also, it allows one to choose, if needed, the dissociation coordinate as the discrete variable. It has been recently shown[13] that the adiabatic energy curves $E_m(R)$ provide a very good zero order description of the resonances. Our whole approach is still based onto the iden-

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tity relation as given by Eq. (1). We will also show that such a numerical continuation can be performed for an arbitrary DVR.

The outline of the paper is as follows. In Sec. II, we first show how one can numerically continue matrix elements $\langle R_p|V|R_{p'}\rangle$ expressed in a DVR, and give a one-dimensional example. This formulation is then used in Sec. III in order to obtain numerically continued multidimensional matrix elements [Eq. (2)]. The method is illustrated on a two dimensional model first introduced by Eastes and Marcus.[14,15] Finally, Sec. IV concludes.

II. ONE DIMENSIONAL FORMULATION

We suppose that the system is to be described in terms of a DVR $\{|\mathscr{R}_p\rangle, p=1,N\}$, related to a finite basis representation (FBR) $\{\varphi_n(R), n=1,N\}$ through the unitary transformation

$$|\mathscr{R}_p\rangle = \sum_{p=1}^{N} U_{pn}|\varphi_n\rangle. \tag{3}$$

The goal of this section is to show how one can obtain the $\langle\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'}\rangle$ matrix elements of the rotated potential $\overline{V}\equiv V(Re^{i\theta})$ from the real ones

$$\langle\mathscr{R}_p|V|\mathscr{R}_{p'}\rangle = V(R_p)\,\delta_{pp'}. \tag{4}$$

One will first derive the formulation in the case of an arbitrary FBR-DVR scheme. The cases of both a uniform grid and an optimized grid will then be studied in more details. The kinetic energy term being analytical, its complex continuation is straightforward, and does not require any particular treatment. For example, in the case of $T_R = -\hbar^2/2\mu d^2/dR^2$, the complex scaled kinetic operator displays matrix elements given by

$$\begin{aligned}\langle\mathscr{R}_p|\overline{T_R}|\mathscr{R}_{p'}\rangle &= e^{-2i\theta}\langle\mathscr{R}_p|T_R|\mathscr{R}_{p'}\rangle \\ &= e^{-2i\theta}[\mathsf{U}.\mathsf{T}.\mathsf{U}^t]_{pp'},\end{aligned}$$

where T is the unscaled kinetic energy matrix expressed in the $\{\varphi_n\}$ basis set.

A. General formulation

Use of identity [Eq. (1)] allows us to write

$$(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'}) = e^{-i\theta}(\widetilde{\mathscr{R}}_p|V|\widetilde{\mathscr{R}}_{p'}), \tag{5}$$

where the $(\cdots|\cdots)$ notation means that the Hermitian conjugation is not used (see the discussion on using the c-product rather than the scalar product in Ref. 16).

The backward rotated $|\widetilde{\mathscr{R}}_p\rangle$ vectors are naturally defined from Eq. (3) as

$$|\widetilde{\mathscr{R}}_p\rangle = \sum_{n=1}^{N} U_{pn}|\widetilde{\varphi}_n\rangle, \tag{6}$$

leading to the expression

$$(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'}) = e^{-i\theta}\sum_{nn'} U_{pn}(\widetilde{\varphi}_n|V|\widetilde{\varphi}_{n'})U_{p'n'}. \tag{7}$$

Because we explicitely consider in this paper the case where no analytic expression is available for the potential, the $(\widetilde{\varphi}_n|V|\widetilde{\varphi}'_n)$ integrals have to be performed numerically. The most convenient way to compute such integrals consists in using a related quadrature scheme (preferably of Gaussian accuracy)

$$(\widetilde{\varphi}_n|V|\widetilde{\varphi}_{n'}) = \sum_{q}^{M} \widetilde{\varphi}_n(R_q)V(R_q)\omega_q\widetilde{\varphi}_{n'}(R_q), \tag{8}$$

where R_q and ω_q correspond, respectively, to the quadrature abscissas and weights.

If one uses for M the same value as the number N of basis functions φ_n, i.e., if the quadrature abcissae $\{R_q\}$ coincidate with the DVR points $\{\mathscr{R}_p\}$, one would obtain erroneous matrix elements. The reason is that the quadrature of Eq. (8) would be exact for nonrotated functions φ_n as long as the relation $n+n'+d^o[V]\leqslant 2M+1$ is satisfied. One has thus to use a quadrature scheme $\{R_q\}$ of dimension higher than that of the DVR $\{\mathscr{R}_p\}$.

At this point, it might be necessary to discuss somewhat about one feature of the DVR method. The basic relation [(Eq. (4)] is a direct consequence of the definition of the $\{\mathscr{R}_p\}$ DVR as the transform of the FBR $\{\varphi_n\}$ given by Eq. (3). In fact, the $\langle\varphi_n|V|\varphi_{n'}\rangle$ matrix elements computed from the associated quadrature scheme

$$\langle\varphi_n|V|\varphi_{n'}\rangle = \sum_{p}^{N} U_{pn}V(R_p)U_{pn'}$$

are not exact for the same reason as discussed previously. However, by the use of the unitary transformation, they lead back to Eq.(4).

By using a higher order quadrature scheme $\{R_q\}$, one can thus achieve an exact evaluation of the $(\widetilde{\varphi}_n|V|\widetilde{\varphi}_{n'})$ matrix elements of Eq. (8). Defining the rectangular complex matrix $\widetilde{\mathsf{U}}$,

$$\widetilde{U}_{qn} = (R_q|\widetilde{\varphi}_n). \tag{9}$$

Equation (8) can be recast into the equivalent DVR type expression,

$$(\widetilde{\varphi}_n|V|\widetilde{\varphi}_{n'}) = \sum_{q}^{M} \widetilde{U}_{qn}V(R_q)\widetilde{U}_{qn'}, \tag{10}$$

which leads to the following relation for the $(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'})$ matrix:

$$(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'}) = e^{-i\theta}[\mathsf{U}\cdot\widetilde{\mathsf{U}}\cdot\mathsf{V}^{(d)}\cdot\widetilde{\mathsf{U}}^t\cdot\mathsf{U}^t]_{pp'}, \tag{11}$$

$\mathsf{V}^{(d)}$ being the real diagonal matrix

$$V^{(d)}_{qq'} = V(R_q)\,\delta_{qq'}. \tag{12}$$

But consequently, the $(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'})$ matrix elements as defined by Eq. (7) are no longer diagonal. This departure from usual DVR properties causes no real problem in the formulation as will be shown in the next subsections. In the case of a one dimensional system, one can question the utility of such a DVR scheme as it does not lead to any advantage

TABLE I. Results for the first two odd resonances of the one dimensional Hamiltonian model [Eq. (13)]. The first column corresponds to an analytic continuation of the potential, the following ones to a numerical continuation by a quadrature using M points. In column 3, a diagonal definition of the DVR was enforced.

		Numerical continuation		
DVR size	Analytical continuation	$M=2N+1$	$M=2N+1$ (diagonal)	$M=N$
$N=18$	$1.42-i8.86(-6)$	$1.42-i4.43(-5)$	…[a]	$1.42-i5.77(-5)$
	$2.60-i1.83(-1)$	$2.53-i1.98(-1)$	$2.645-i0.61(-1)$	…[a]
$N=24$	$1.42-i5.84(-4)$	$1.42-i5.87(-4)$	$1.37-i1.63(-3)$	$1.42-i6.23(-4)$
	$2.59-i1.74(-1)$	$2.59-i1.79(-1)$	$2.60-i0.41(-1)$	$2.65-i1.04(-1)$
$N=29$	$1.42-i5.83(-4)$	$1.42-i5.83(-4)$	$1.37-i1.35(-3)$	$1.42-i6.21(-4)$
	$2.58-i1.74(-1)$	$2.58-i1.74(-1)$	$2.61-i0.42(-1)$	$2.66-i1.71(-1)$

[a]Resonance position unassignable.

compared to a direct FBR formulation. Its actual interest will appear in Sec. III when dealing with multidimensional systems.

B. One dimensional test case

As a first application of the above formulation, we consider the case of an equidistant grid

$$\{R_p \equiv p.\Delta R,\ \ p=1,N\}. \tag{13}$$

[A system can always be translated such that its domain of interest lies between 0 and $R_{\max}=(N+1)\Delta R$.] The associated DVR $\{\mathscr{R}_p, p=1,N\}$ is the conjugate representation of the sine basis set $\{\varphi_n, n=1,N\}$,[17,18]

$$\varphi_n(R)=\sqrt{\frac{2}{(N+1)\Delta R}}\sin\frac{n\pi R}{(N+1)\Delta R} \tag{14}$$

eigenstates of the $[0,R_{\max}]$ box. These two representations are related through the unitary transformation Eq. (3) where

$$U_{pn}=\sqrt{\frac{2}{(N+1)}}\sin\frac{n\pi R_p}{(N+1)\Delta R}. \tag{15}$$

In order to test our formulation, we present now a simple calculation aimed at determining the resonances of the model Hamiltonian

$$H=T+V=-\frac{1}{2}\frac{d^2}{dR^2}+(R^2-0.8)e^{-0.1R^2}+0.8 \tag{16}$$

already studied by Moiseyev *et al.*[19] and Korsch *et al.*[20] This system displays a single bound state around $E=0.5$ and a string of resonances $\{E_{\rm res}^{(m)}, m=1,2,\ldots\}$. In order to obtain the odd ones, one can restrict the domain to $[0,\infty[$ and use a basis set of functions $\{\varphi_n(R)\}$ which all satisfy the boundary condition $\varphi_n(0)=0$, such as the sine basis of Eq (14). In this study, we will focus on the lowest two odd resonances $E_{\rm res}^{(1)}$ and $E_{\rm res}^{(3)}$. Two series of calculations, presented in Table I, have been performed. In each case, the dimension N of the $\{\mathscr{R}_p\}$ DVR has been varied while the box size was kept at the value $R_{\max}=15$. In the first series, used as a reference and shown in column 1, we employed the *analytic* expression of the potential and defined the scaled Hamiltonian matrix elements in the DVR as

$$(\mathscr{R}_p|\overline{H}|\mathscr{R}_{p'})=-\frac{1}{2}e^{-2i\theta}\langle\mathscr{R}_p|\frac{d^2}{dR^2}|\mathscr{R}_{p'}\rangle + V(R_p e^{i\theta})\,\delta_{pp'}. \tag{17}$$

The next three columns display results obtained from a numerical continuation of the potential V by means of Eq. (7,10), with

$$(R_q|\tilde{\varphi}_n)=\sqrt{\frac{2}{M+1}}\sin\frac{n\pi R_q e^{-i\theta}}{R_{\max}}. \tag{18}$$

Column 2 corresponds to using a quadrature grid $\{R_q\}$ twice as dense as the $\{|\mathscr{R}_p\rangle\}$ DVR, explicitly retaining in the calculation the *nondiagonal* terms $(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'})$. Column 3 differs from column 2 in that these off diagonal terms were discarded in the calculation. Finally, column 4 also corresponds to retaining the non diagonal terms but using a quadrature grid identical to that of the initial DVR.

The main conclusion which emerges from these calculations is that the proposed numerical continuation scheme is able to reproduce the correct results, provided the off diagonal terms $(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'})$ are explicitly retained in the formulation. In fact, the $M=N$ calculations with these terms lead to better results than those using the dense quadrature grid $(M=2N+1)$ but a diagonal $\overline{V}$ definition. As will be shown in Sec. III, these off diagonal terms pose no problem and still allow one to use the DVR formulation in conjunction with an adiabatic reduction of the basis.

C. Optimization of the DVR scheme

As shown above, a sine-based DVR allows for an easy primary description of a complex scaled potential. This is equivalent to the very general role played by the plane wave basis set for time dependent wave packets, due to the underlying FFT scheme.[21] However, for a Morse potential such as the one associated to the two-dimensional model studied in Sec. III, it constitutes a poor representation in terms of efficiency. The reason is that the spacing between grid points is dictated by the maximum kinetic energy allowed, which corresponds to the bottom of the well. In the asymptotic region, where the de Broglie wavelength can be considerably larger, one could use in principle a much broader mesh size.

A solution to this problem was proposed 30 years ago by Harris, Engerholm, and Gwinn (HEG).[22] They showed that if $\{\varphi_n\}$ is some basis set, one can use the eigenvalues $\{R_p\}$ of the position matrix $\langle\varphi_n|\hat{R}|\varphi_{n'}\rangle$ in order to numerically evaluate the matrix elements of any function $f(R)$,

$$\langle\varphi_n|f(R)|\varphi_{n'}\rangle=\sum_p U_{pn}f(R_p)U_{pn'}, \tag{19}$$

where U is the associated eigenvector matrix. It was later shown by Dickinson and Certain[23] that this method was equivalent to a quadrature scheme of Gaussian accuracy. The HEG method thus provides a way to define a numerical quadrature when no analytic expression is known for the eigenfunctions $\{\varphi_n\}$, or when it is too cumbersome to deal with.

Analyzed in terms of the DVR formulation, the HEG method allows for the definition of a DVR $\{|\mathscr{R}_p\rangle\}$, conjugate to the $\{\varphi_n\}$ FBR,

$$|\mathscr{R}_p\rangle=\sum_n U_{pn}|\varphi_n\rangle, \tag{20}$$

which satisfies the basic relation

$$f(R)|\mathscr{R}_p\rangle=f(R_p)|\mathscr{R}_p\rangle. \tag{21}$$

This property was later used by Leforestier[24] and Echave and Clary[25] in order to define an adapted DVR to some zero-order Hamiltonian H^0, the eigenfunctions of which being precisely the $\{\varphi_n\}$ basis set.

The $(\mathscr{R}_p|V|\mathscr{R}_{p'})$ matrix elements appearing in the HEG formulation can be numerically continued by means of Eq. (7,10), provided one can express the $(R_q|\widetilde{\varphi}_n)$ terms. This can be realized, for example, by first computing the $\{\varphi_n\}$ eigenstates of interest in the primary sine basis set $\{|S_m\rangle, m=1,M\}$ conjugate to the dense $\{|R_q\rangle\}$ DVR,

$$|\varphi_n\rangle=\sum_m T_{mn}|S_m\rangle. \tag{22}$$

(In order to carry on the HEG procedure, one has to truncate the $\{\varphi_n\}$ basis set, otherwise the HEG representation $\{|\mathscr{R}_p\rangle\}$ would be strictly identical to the primary DVR $\{|R_q\rangle\}$.) The $(R_q|\widetilde{\varphi}_n)$ terms can then be explicited as

$$(R_q|\widetilde{\varphi}_n)=\sum_m T_{mn}(R_q|\widetilde{S}_m), \tag{23}$$

with

$$(R_q|\widetilde{\varphi}_m)=\sqrt{\frac{2}{M+1}}\sin\frac{m\pi R_q e^{-i\theta}}{R_{\max}}. \tag{24}$$

Similarly, the scaled kinetic matrix elements in the HEG DVR can be computed from those in the primitive sine $\{S_m\}$ basis set

$$\begin{aligned}(\mathscr{R}_p|\overline{T_R}|\mathscr{R}_{p'})&=\sum_{nn'} U_{pn}(\varphi_n|\overline{T_R}|\varphi_{n'})U_{p'n'}\\&=e^{-2i\theta}\sum_{nmn'} U_{pn}T_{mn}(S_m|T_R|S_m)T_{mn'}U_{p'n'}.\end{aligned} \tag{25}$$

D. Discussion

With the use of Eq. (10), Eq. (5) can be cast into the DVR type expression,

$$\begin{aligned}(\mathscr{R}_p|\overline{V}|\mathscr{R}_{p'})&=e^{-i\theta}(\widetilde{\mathscr{R}}_p|V|\widetilde{\mathscr{R}}_{p'})=e^{-i\theta}\sum_q^M(\widetilde{\mathscr{R}}_p|R_q)\\&\quad\times(R_q|V|R_q)(R_q|\widetilde{\mathscr{R}}_{p'}).\end{aligned} \tag{26}$$

As discussed in Sec. II A, the quadrature (involving the R_q points) is performed on a grid *denser* that the one $\{\mathscr{R}_p\}$ of final interest. This equation shows that the complex scaled matrix elements in a DVR can be obtained from the unscaled elements computed in a related (denser) DVR. The method we developed previously allowed us to compute the $(R_q|\widetilde{\mathscr{R}}_p)$ quantities by using some intermediate basis set $\{\varphi_n\}$,

$$(R_q|\widetilde{\mathscr{R}}_p)=\sum_n U_{pn}(R_q|\widetilde{\varphi}_n) \tag{27}$$

in which the backward rotation can be carried out. In the case of an equidistant DVR $\{|\mathscr{R}_p\rangle\}$, the $\{\varphi_n\}$ correspond to sine functions. In the HEG case, the $\{\varphi_n\}$ correspond to numerical eigenstates of some zero order Hamiltonian H^0, and one has to perform one more step

$$(R_q|\widetilde{\mathscr{R}}_p)=\sum_{nm} U_{pn}T_{mn}(R_q|\widetilde{S}_m) \tag{28}$$

in order to reach the analytic sine basis set $\{S_m\}$.

III. MULTIDIMENSIONAL FORMULATION

Bačić and Light[11] have shown that a basis, supposed here to depend only on the two variables R and r for sake of clarity, can be very efficiently contracted as described now. Let us write the total Hamiltonian as

$$H=T_R+h, \tag{29}$$

where $h=T_r+V(R,r)$ displays no differential operator with respect to R. One defines an adiabatic basis $\{|\Phi_m(R_p)\rangle, m=1,M_p\}$, solution of the fixed R Hamiltonian $h(R_p)$,

$$h(R_p)|\Phi_m(R_p)\rangle=\mathscr{E}_m(R_p)|\Phi_m(R_p)\rangle. \tag{30}$$

By using a DVR $\{|\mathscr{R}_p\rangle, p=1,N\}$ for the R variable, one can contract the initial basis set into the new one $\{|\Phi_m(R_p)\rangle|\mathscr{R}_p\rangle\equiv|\Phi_m^{(p)},\mathscr{R}_p\rangle\}$. [From now on, we will use the notation $|\Phi_m^{(p)}\rangle\equiv|\Phi_m(R_p)\rangle$.] In this contracted basis set, the Hamiltonian operator H displays the following matrix elements:

$$\langle \mathscr{R}_p, \Phi_m^{(p)} | H | \Phi_{m'}^{(p')}, \mathscr{R}_{p'} \rangle = \langle \mathscr{R}_p | T_R | \mathscr{R}_{p'} \rangle \langle \Phi_m^{(p)} | \Phi_{m'}^{(p')} \rangle + \mathscr{E}_m^{(p)} \delta_{mm'} \delta_{pp'}. \tag{31}$$

Lipkin *et al.*[6] have used this formulation in order to reduce as much as possible the basis set size prior to diagonalization of the complex scaled Hamiltonian matrix. In the contracted basis set, the complex scaled Hamiltonian operator displays matrix elements given by

$$\langle \mathscr{R}_p, \Phi_m^{(p)} | \overline{H} | \Phi_{m'}^{(p')}, \mathscr{R}_{p'} \rangle = \langle \mathscr{R}_p | \overline{T_R} | \mathscr{R}_{p'} \rangle \langle \Phi_m^{(p)} | \Phi_{m'}^{(p')} \rangle + \langle \Phi_m^{(p)} | \overline{h(R_p)} | \Phi_{m'}^{(p')} \rangle \delta_{pp'}. \tag{32}$$

This formulation explicitly relied on an analytical expression of the potential $V(R,r)$ entering h.

Recently, this approach was extended by Ryaboy and Moiseyev to the case of a nondilation analytic potential. Analyzed in terms of the above two dimensional formulation, their approach would consist in first computing the complex scaled Hamiltonian $h(\overline{r,R_p})$ at fixed R using a sine basis set for r, r being the dissociation coordinate. The corresponding matrix elements were obtained by means of the identity relation (1) using backward scaled sine functions $\varphi_i(re^{-i\theta})$ and a quadrature rule. Diagonalization of the resulting matrix lead to complex scaled ray-eigenstates $\{|\overline{\Phi}_m(R_p)\rangle\}$, to be used as the basis set for the r variable. The overall basis set was then defined as $\{|\overline{\Phi}_m^{(p)}\rangle | \mathscr{R}_p \rangle\}$. The formulation we propose aims at obtaining the complex scaled matrix elements in terms of the unscaled ones as given by Eq. (31). It will focus on the $\overline{h}$ term of Eq. (32), as the kinetic energy operator T_R poses no problem, and can be treated as shown in Sec. II.

A. General formulation

Starting from the expression [see Eq. (30)],

$$h = \sum_m |\Phi_m(R)\rangle \mathscr{E}_m(R) \langle \Phi_m(R)|, \tag{33}$$

one can write

$$\begin{aligned}(\mathscr{R}_p | \overline{h} | \mathscr{R}_{p'}) &= e^{-i\theta} (\widetilde{\mathscr{R}}_p | h | \widetilde{\mathscr{R}}_{p'}) \\ &= e^{-i\theta} \sum_m (\widetilde{\mathscr{R}}_p | \{ |\Phi_m(R)\rangle \mathscr{E}_m(R) \\ &\quad \times \langle \Phi_m(R)| \} | \widetilde{\mathscr{R}}_{p'}).\end{aligned} \tag{34}$$

In the above expression, the terms between brackets $\{\cdots\}$ can be considered as a function of R. As discussed in Sec. II A, one should evaluate the integral over R by using a quadrature scheme defined on a grid $\{R_q, q=1,M\}$ denser than the DVR $\{\mathscr{R}_p, p=1,N\}$ of interest. This can be realized by using twice the closure relation $1=\Sigma_q^M |R_q\rangle\langle R_q|$, leading to the equivalent form

$$(\mathscr{R}_p | \overline{h} | \mathscr{R}_{p'}) = e^{-i\theta} \sum_{mq} (\widetilde{\mathscr{R}}_p | R_q) | \Phi_m^{(q)} \rangle \mathscr{E}_m^{(q)} \times \langle \Phi_m^{(q)} | (R_q | \widetilde{\mathscr{R}}_{p'}). \tag{35}$$

One finally obtains for the matrix elements of $\overline{h}$ in the $\{|\Phi_m^{(p)}, \mathscr{R}_p\rangle\}$ basis set

$$\begin{aligned}&(\mathscr{R}_p, \Phi_m^{(p)} | \overline{h} | \Phi_{m'}^{(p')}, \mathscr{R}_{p'}) \\ &= e^{-i\theta} \sum_{m''q} (\widetilde{\mathscr{R}}_p | R_q) \langle \Phi_m^{(p)} | \Phi_{m''}^{(q)} \rangle \mathscr{E}_{m''}^{(q)} \langle \Phi_{m''}^{(q)} | \Phi_{m'}^{(p')} \rangle \\ &\quad \times (R_q | \widetilde{\mathscr{R}}_{p'}).\end{aligned} \tag{36}$$

The above equation is quite general, and demonstrates that multidimensional matrix elements expressed in a contracted basis set can be numerically continued for complex scaling calculations. As emphasized before, the off diagonal terms of $\overline{h}$ have to be explicitly retained in the formulation. It should be noted that the actual definition of the DVR chosen for the dissociation coordinate R only appears through the $(R_q | \widetilde{\mathscr{R}}_p)$ terms [see Eq. (27)–(28)].

We shortly discuss now the computational cost of this formulation. The overlap terms $\langle \Phi_m^{(p)} | \Phi_{m''}^{(q)} \rangle$ appearing in Eq. (36) are also required in the original formulation, associated to the kinetic operator matrix elements [see Eq. (32)]. As a consequence, they do not lead to any new calculation. The extra cost comes uniquely from the necessity to use a denser grid $\{R_q\}$ in order to perform the numerical continuation. This in turn implies to perform the ray-eigenstate calculation on this dense grid associated to the adiabatic variable R. As will be shown in Sec. III B, it typically increases by a factor 1.5 about this preconditionning step, as compared to the hypothetical case where an analytic expression of the potential is available.

B. Application to the Eastes–Marcus model

As a way to check the new formulation in a multidimensional case, we applied it to the well studied Eastes–Marcus model.[14,15] It can be viewed as representing a dissociative colinear triatomic molecule

$$[ABC]^* \rightarrow A + BC(v),$$

and consists in an harmonic oscillator (BC) coupled to a Morse potential $(A-BC)$,

$$\begin{aligned}&H = -\frac{1}{\mu}\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + D[e^{-\alpha(x-y)}-1]^2 + y^2 - D, \\ &\mu = 0.2, \quad \alpha = 0.05, \quad D = 1.5.\end{aligned} \tag{37}$$

According to Bačić and Light,[11] one first preconditions the basis set by computing the adiabatic solutions at fixed x_p values

$$\left\{ -\frac{\partial^2}{\partial y^2} + D[e^{-\alpha(x_p-y)}-1]^2 - D + y^2 \right\} \Phi_m^{(p)}(y) = \mathscr{E}_m^{(p)} \Phi_m^{(p)}(y). \tag{38}$$

TABLE II. Comparison of the characteristics of the first two resonances of the Eastes–Marcus model, as obtained by either an analytic or numerical continuation of the potential.

DVR size	HEG grid (anal. cont.)	HEG grid (num. cont.)
$N=30$	$1.639\,01-i2.2(-7)$	$1.639\,01-i1.7(-7)$
	$1.887\,03-i1.2(-6)$	$1.887\,03-i6.9(-7)$
$N=40$	$1.639\,01-i2.0(-7)$	$1.639\,01-i1.9(-7)$
	$1.887\,03-i1.0(-6)$	$1.887\,03-i9.7(-7)$
$N=50$	$1.639\,01-i2.0(-7)$	$1.639\,01-i2.0(-7)$
	$1.887\,03-i1.0(-6)$	$1.887\,03-i9.8(-7)$
$N=60$	$1.639\,01-i2.0(-7)$	$1.639\,01-i2.0(-7)$
	$1.887\,03-i1.0(-6)$	$1.887\,03-i1.0(-6)$

This first step has been realized using a DVR $\{|y_s\rangle, s=-S,S\}$ for the BC-oscillator,

$$|\Phi_m^{(p)}\rangle=\sum_s T_{sm}^{(p)}|y_s\rangle. \tag{39}$$

This procedure allows for a simplified calculation of the overlap terms $\langle\Phi_m^{(p)}|\Phi_{m'}^{(q)}\rangle$ entering Eq. (36) as

$$\langle\Phi_m^{(p)}|\Phi_{m'}^{(q)}\rangle=\sum_s T_{sm}^{(p)}T_{sm'}^{(q)}. \tag{40}$$

The final two dimensional basis set reads as $\{|\Phi_m^{(p)},X_p\rangle\}$, where $\{|X_p\rangle\}$ stands for the HEG representation. As discussed in Sec. II C, it was obtained by diagonalizing the $\hat{x}$ operator in the truncated basis set of the eigenstates $\{\phi_n(x)\}$ of the following zero order Hamiltonian:

$$\hat{h}^0=-\frac{1}{\mu}\frac{\partial^2}{\partial x^2}+D\{e^{-\alpha x}-1\}^2-D. \tag{41}$$

We also made use of a uniform DVR $\{|x_q\rangle\}$, as the working basis set to express the eigenstates $\{\phi_n(x)\}$, as well as the dense DVR appearing in Eq. (36).

We present in Table II a comparison of the first two resonances as computed either by analytic or numerical continuation of the potential. While using always the same box size $(-20\rightarrow 150)$ for x, different grid dimensions have been used, corresponding to an increasing accuracy on the resonance widths. First, one can remark that the resonance positions are fully converged to a 6 digit accuracy in both sets of calculations. As could be expected, the widths obtained by analytic continuation converge first $(N=40)$, but the results coming out of the numerical scheme display a relative error of only 5% for the same grid size. The important point is that by increasing the dimension of the scheme, the numerical results eventually converge onto the exact ones, as shown in the table. The accuracy needed in the calculations of molecular resonances will be further addressed below, in the Conclusions.

IV. CONCLUSION

We have presented a procedure which allows one to numerically continue the matrix elements of any real Hamiltonian operator expressed in a discrete variable representation. One thus avoids the need of a *global* analytical expression of the potential, and can use instead a piecewise one, such as the spline interpolation method. When applied to the multidimensional case, one can first precondition the basis set, using Bačić and Light SAR method[11] with the real potential, and then numerically continue the resulting matrix elements. It constitutes an extension of the method initially proposed by Moiseyev and Corcoran[7] to a multidimensional DVR type basis set. Its interest stems from the fact that the SAR method produces an optimum contracted basis set in order to handle molecular systems. Also, it allows the dissociation coordinate to be treated by a grid adapted to the variation of the de Broglie wavelength, by means of the HEG method.[22]

We now address the accuracy achieved by our numerical procedure on the Eastes–Marcus model. Considering the minimal basis set size $(N=40)$ which leads to converged results when using an analytical continuation of the potential, the resonance positions come out with a 6 digit accuracy through numerical continuation. However, the associated widths display a relative error of $\sim$0.5%. We would first like to point out that in most cases, such a precision is amply sufficient for *numerical* molecular potentials, as those obtained from *ab initio* calculations. In fact, the intrinsic errors due to such potentials can be expected to overwhelm those associated to the numerical continuation procedure. A second point concerns the fact that this numerical scheme is well behaved. By increasing the number of points used, the results eventually converge onto the exact ones.

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