COMPLEX SCALING METHOD FOR NUMERICAL POTENTIALS

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The method of complex scaling transformation can be extended to either numerical or sophisticated piecewise inhomogeneous potentials, incorporating the use of several well-established transformation theories and stable quadrature algorithms. The method is illustrated by a study of the multichannel rotational predissociations of Ar, N₂ van der Waals molecules, using tabulated numerical anisotropic potentials.

1. Introduction

The method of complex scaling transformation [1], which allows one to describe the resonance features in the continuous spectrum by employing only bound-state techniques, is an active field of current research in atomic and molecular physics [2]. For most, if not all, of the systems studied so far, the potentials used are exclusively in simple homogeneous analytic forms to which the complex scaling transformation $R \rightarrow R e^{i\alpha}$ can be directly applied. However, in the case of molecular problems, very often accurate potential surfaces are available only in tabulated numbers rather than in specified analytic forms. There is no previous demonstration that the complex scaling transformation can be applied successfully to numerical potentials. We advance in this paper a stable computational scheme which retains the accuracy of the numerical potential data (without fitting them into arbitrary analytic forms) and preserves the dilatation analyticity of the complex scaling transformation. This generalizes the scope of the utility of the method of complex scaling. A preliminary brief report of this method has been presented in the XII ICPEAC [3].

2. Complex scaling method for numerical potentials

Let \{\phi_i(R)\} be an appropriate $L^2$ (square integrable) basis set for a specific problem under consideration. One of the main efforts in complex scaling calculations is to compute the matrix elements of the complex-rotated potential $V(R e^{i\alpha})$ [obtained by applying $R \rightarrow R e^{i\alpha}$ to the potential $V(R)$], namely $\langle \phi_i(R) | V(R e^{i\alpha}) | \phi_j(R) \rangle$, efficiently and reliably. However, in the case that $V(R)$ are only given in tabulated numerical forms or in some sophisticated analytical forms (other than the simple exponential or inverse powers of $R$), it is not obvious how one can compute these complex matrix elements directly and accurately. For example, a straightforward application of the complex coordinate transformation to the cubic–spline interpolated complex numerical potentials indicates the dilatation analyticity is badly destroyed [4].

To bypass these numerical instabilities, we present a method which takes advantage of several well-established transformation theories and stable quadrature algorithms. The procedure consists of the following three steps:

Step (i). The identity

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\(<\phi_j(R)|V(R)|\phi_j(R)\rangle = e^{-i\alpha}\langle\phi_j(Re^{-i\alpha})|V(R)|\phi_j(Re^{-i\alpha})\rangle\)

is used to transform the complex rotated potential back to the real potential.

**Step (ii).** The inner projection technique [5] is adopted such that

\(<\phi_j(Re^{-i\alpha})|V(R)|\phi_j(Re^{-i\alpha})\rangle = \sum_{mn} \langle\phi_j(Re^{-i\alpha})|\psi_m(R)\rangle \langle\psi_m(R)|V(R)|\psi_n(R)\rangle \langle\psi_n(R)|\phi_j(Re^{-i\alpha})\rangle\).

where \(\{\psi_m(R)\}\) are real, \(L^2\)-orthonormal basis functions. The simplifying feature here is that the evaluation of the complex-scaled hamiltonian matrix is now replaced by the much simpler calculations of complex overlap matrix, as well as the matrix elements of real potentials. For several of the orthonormal basis sets we have used so far, such as harmonic oscillator, Laguerre, gaussian, etc., the complex overlap matrix elements \(\langle\phi_j(Re^{-i\alpha})|\psi_m(R)\rangle\) can be derived in closed analytic forms and evaluated exactly [4]. Thus the uncertainty associated with the complex rotated potentials can be completely removed.

**Step (iii).** The matrix elements of the real potential \(V(R)\), in numerical or sophisticated analytical form, \(\langle\phi_j(R)|V(R)|\phi_j(R)\rangle\), can also be evaluated accurately by using the well-known transformation theory and quadrature scheme introduced by Harris et al. [6].

The abovementioned three-step transformation procedure allows us to expand the scope of the method of complex scaling to virtually any system. We have tested this procedure against one of our previous studies [7] of rotational predissociation of some model atom–diatom van der Waals molecules involving (analytical) Lennard–Jones (LJ) type potentials. It was found [4] that the results for numerical LJ potentials are essentially in complete agreement with the previous data for analytical LJ potentials. Recently this method has also been applied successfully to the study of rotational predissociation of inert-gas–\(H_2\) van der Waals molecules involving sophisticated inhomogeneous and piecewise analytical potentials [8]. We shall now proceed to the application of this method to the multichannel rotational predissociation of \(Ar...N_2\) van der Waals molecules using the accurate numerical potential surfaces obtained recently by Lee and Kim [9].

### 3. Multichannel rotational predissociation of \(Ar...N_2\) van der Waals molecules — a case study

In this section we shall apply the transformation and quadrature procedures obtained in section 2 along with the coupled-channel complex-coordinate (CCCC) formalism [7,10] to the calculation of the rotational predissociation lifetimes of \(Ar...N_2\) van der Waals molecules. The system under consideration consists of a diatomic rigid rotor \(N_2\) with orientation \(r\) and an \(Ar\) atom with position \(R\) relative to the center of mass of the diatom. The hamiltonian for the \(Ar-N_2\) complex, within the Born–Oppenheimer approximation, can be represented by [11]

\[H(R, \theta) = \left\{-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2I_{rot}^2}(\hat{R})^2 \right\} + V(R, \theta).\]

In this equation \(\mu\) is the reduced mass of \(Ar-N_2\), \(\cos \theta = r \cdot \hat{R}, B_{rot}\) the rotational constant of the diatom, \(I\) the rotational angular momentum of \(N_2\), \(\hat{R}\) the orbital angular momentum of \(N_2\) and \(Ar\) about each other, and \(V(R, \theta)\) the interaction potential of \(Ar\) and \(N_2\). Lee and Kim [9] have recently obtained the \(Ar...N_2\) potential surface using their modified electron gas model. The potential is expanded in terms of Legendre polynomials:

\[V(R, \theta) = V_0(R) + V_2(R)P_2(\cos \theta) + V_4(R)P_4(\cos \theta),\]

where the radial potentials \(V_k(R)\) are given in tabulated numerical forms [9] and are shown in fig. 1.

The predissociation resonances associated with the atom–rigid-rotor diatomic complex can be qualitatively understood as follows. During a low-energy molecular collision, the kinetic energy of relative motion can be converted into internal (rotational) excitation and the attractive mutual interaction between the excited molecules can then lead to a temporary formation of a metastable van der Waals complex. The width of the resonance is associated with the dissociation of the van der Waals molecule which occurs when the internal energy is reconverted.
The radial potentials $V_k(R)$ ($k = 0, 2, 4$), of the Ar-N$_2$ system [cf. eq. (4)] are the approximate analytically fitted potentials of ref. [12].

The dotted lines (b) are the numerical potentials of Lee and Kim [9] and the solid curves (J) are the potential curves of the Ar-N$_2$ system. $V_0(R)$ is the isotropic potential, $J$ is the rotational quantum number of N$_2$, and $I$ is the relative orbital angular momentum of Ar and N$_2$. $E(I)$ is the diatomic level energies ($B_{rot} = 2.01$ cm$^{-1}$) shown here are the zero-coupling limit level energies for the angular channels contributing to $J= M = 0$ states of the Ar-N$_2$ complex.

The matrix elements for the complex scaled hamiltonian $H_\alpha(R, \theta)$ obtained by applying $R \rightarrow R e^{i\theta}$ to the real hamiltonian $H(R, \theta)$ in the $|\gamma n\rangle$ representation is [7].

$$
\langle \gamma' n' | H_\alpha(R, \theta) | \gamma n \rangle = e^{-2i\theta} \langle h_\alpha | x_{\gamma} (R) | l(l+1)/R^2 + h_\alpha | x_{\gamma} (R) | l(l+1)/R^2 \rangle + B_{rot}(l+1)\delta_{II'}\delta_{JJ'}\delta_{MM'} + \sum_{k=0,2,4} \langle x_{\gamma} | V_k(R e^{i\theta}) | x_{\gamma} (R) \rangle f_k(l', J, J') \delta_{JJ'}\delta_{MM'},
$$

where $f_k$ is the Percival-Seaton coefficient [13]. The resulting matrix of $H_\alpha$ is a symmetric complex matrix whose complex eigenvalues can be determined via the secular determinant.
The desired metastable states are then identified by the stationary points [2,7] of the \( \alpha \) trajectories of complex eigenvalues.

In order to demonstrate the numerical procedure, we shall focus on the study of the metastable states which correlate with the isotropic channel \([7] j = l = 8, J = M = 0\) of the Ar \(\cdot N_2\) complex (see fig. 2). Because of the symmetry of \(N_2\), only the following angular basis (with \(J = M = 0\)) need be considered in the coupled-channel calculation.

\( (j = 0, l = 0), \quad (j = 2, l = 2), \quad (j = 4, l = 4), \quad ... \)

For the present case, we found that the resonance energies and widths (lifetimes) of the metastable states can be determined accurately by including all the four open channels \((j = l = 0, 2, 4, 6, J = M = 0)\), and at least two closed channels \((j = l = 8, 10, J = M = 0)\) (cf. fig. 2). The matrix structure in the \(|\gamma n\rangle\) representation [eq. (5)] is of \(N_c \times N_c\) block form (where \(N_c\) is the number of coupled channels included in the calculation) as depicted in fig. 3. Within each diagonal block specified by the channel quantum number \(\gamma = (JM)\), an appropriate orthonormal harmonic oscillator (HO) type \(L^2\) basis will be used to expand the radial wavefunction. It is well known [14] that the HO basis provides a compact analytic representation for the complete set of bound and continuum states of an anharmonic oscillator.

The HO basis previously used for problems of molecular predissociation [7] and intense field molecular photodissociation [15] involving homogeneous analytic potentials has the following form

\[
\chi_n(R) = \left(\beta n^{1/2} 2^n n!\right)^{1/2} H_n(\beta(R - R_0)) \exp\left[-\frac{1}{2}\beta^2(R - R_0)^2\right], \quad n = 1, 2, ..., N, \gamma
\]

where \(H_n\) is a Hermite polynomial, and \(\beta\) and \(R_0\) are adjustable parameters. This functional form, however, is not the most convenient one for the current study. The reason is the complex overlap matrix elements \(\langle \chi_n(R)e^{-i\alpha} | \chi_m(R) \rangle\) in step (u) of section 2 in the \(R\)-rotation method (i.e. \(R \rightarrow Re^{i\alpha}\)), though can be worked out in closed analytic form, involves sophisticated triple summations [4] and cannot be evaluated efficiently.

We discuss here an alternative but more efficient procedure (which we shall call the \(X\)-rotation method) which is capable of reducing the complex overlap matrix element expression into a single summation formula [4,8]. In this procedure, we rewrite the potential \(V(R)\) as \(V(X + R_0)\) where \(X = R - R_0\) and \(R_0\) is an adjustable constant usually chosen to be somewhat larger than the equilibrium distance of the isotropic potential \(V_0(R)\). The appropriate complex scaling in the \(X\)-rotation method is to scale \(X\) rather than \(R\):

\[
V(X + R_0) = V(Re^{i\alpha} + R_0).
\]
and the basis function $\psi_n(x)$ has the same form as eq. (8) except with only one adjustable parameter $\beta$ (the other parameter $R_0$ has now been absorbed into the potential function itself):

$$\psi_n(x) = (\beta\alpha)^{1/2}2^nn!1/2H_n(\beta x)\exp(-\beta x^2).$$

(9)

Before going on the implementation of the $X$-rotation method, we discuss here some of the justification of this alternative procedure. Formally speaking, the potential $V(X + R_0)$ with the shifted coordinate $X$ is just an alternative way of representing the original potential function $V(R)$. For problems where $X$ is closely related to some real physical properties of the system, the $X$-rotation method has been found to be particularly fruitful [4]. For example, in the study of multichannel rotational predissociation of inert-gas-H$_2$ van der Waals molecules, we found the $X$-rotation method works much better than the $R$-rotation method for systems involving sophisticated inhomogeneous and piecewise analytic potentials [8]. This may be partially attributed to the fact that for potentials involving harmonic oscillator type wells, $X$ is perhaps the more natural coordinate than $R$ for describing the vibrational stretching of the van der Waals bond.

To test the idea that the $X$- and $R$-rotation methods should give rise to the same physical results, we have also previously carried out [15] a study of the problem of the tunneling in the anharmonic oscillator

$$V(X) = \frac{1}{4}x^2 - \lambda X^3,$$

(10)

which was used by Yaris et al. [16] and by Atabek and Lefebvre [17] to experiment with the complex scaling methods. We found [15] that the resonance energies and widths computed with the $X$-rotation method and the $X$-rotated potential

$$V(Xe^{i\alpha}) = \frac{1}{4}x^2 - \lambda e^{3i\alpha}x^3$$

(11)

are essentially identical to the results obtained by the $R$-rotation method and the $R$-rotated potential ($X = R - R_0$)

$$V(Re^{i\alpha}) = \frac{1}{4}(Re^{i\alpha} - R_0)^2 - \lambda(Re^{i\alpha} - R_0)^3.$$  

(12)

An example of the calculation is given in table 1.

We now return to the implementation of the $X$-rotation method using the HO basis [eq. (9)]. The non-vanishing complex overlap matrix elements can be worked out analytically [4] and computed efficiently ($m, n$ are integers).

$$\langle X_{mn}(Xe^{i\alpha})|X_{nm}(X)\rangle = (-1)^{m-n}1^{n+m}e^{i\alpha/2}2^{-(n+m)}[(2m)(2n)!]^{1/2}(\tan \alpha)^{n+m}(\cos \alpha)^{-1/2}$$

$$\times\sum_{r=0}^{\min(m,n)}(2i\sin \alpha)^{2r}[(n-r)(n-r)!](2r)!^{-1}. \quad (13a)$$

Table 1

<table>
<thead>
<tr>
<th>$N$</th>
<th>$X$ rotation</th>
<th>$R$ rotation</th>
<th>Finite differences</th>
</tr>
</thead>
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<tr>
<td></td>
<td>(this work)</td>
<td>(this work)</td>
<td>(ref. [17])</td>
</tr>
<tr>
<td>0</td>
<td>0.48567937 - 0.236698 x 10$^{-5}$</td>
<td>0.48567937 - 0.236698 x 10$^{-5}$</td>
<td>0.4856786 - 0.30 x 10$^{-5}$</td>
</tr>
<tr>
<td>1</td>
<td>1.3915748 - 0.134193 x 10$^{-2}$</td>
<td>1.3915748 - 0.134193 x 10$^{-2}$</td>
<td>1.391572 - 0.13425 x 10$^{-2}$</td>
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<td>2</td>
<td>2.1321356 - 0.687626 x 10$^{-1}$</td>
<td>2.1321356 - 0.687626 x 10$^{-1}$</td>
<td>2.13213 - 0.68762 x 10$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>2.817874 - 0.363974 i</td>
<td>2.817874 - 0.363974 i</td>
<td>2.81786 - 0.363967 i</td>
</tr>
<tr>
<td>4</td>
<td>3.586675 - 0.777257 i</td>
<td>3.586675 - 0.777257 i</td>
<td>3.58665 - 0.77724 i</td>
</tr>
</tbody>
</table>

a) The corresponding harmonic oscillator (HO) quantum number.
b) Calculated using eq. (11) and 40 HO basis functions ($\omega = 7.0 s_0^{-1}$ and $\alpha = 0.30$ rad).
c) Calculated with eq. (12) and 40 HO basis functions ($\omega = 7.0 s_0^{-1}$, $R_0 = 1.0 s_0$ and $\alpha = 0.3$ rad).
and
\[ \langle x_{2m+1}(X+\alpha)X_{2n+1}(X) \rangle = (-1)^{m} \left( \frac{m+n+2}{2} \right)^{2} \left( \frac{(2m+1)!}{(2n+1)!} \right)^{1/2} \left( \tan \alpha \right)^{m+n+1} \left( \cos \alpha \right)^{-1/2} \]
\[ \times \sum_{t=0}^{\min(m,n)} \left( \frac{2}{\sin \alpha} \right)^{2n+1} \left( m-t \right)! \left( n-t \right)! \left( 2t+1 \right)! \right]^{-1}. \]  

(13b)

Finally, the matrix elements of the real potentials \( V_k(X + R_0) \) (\( k = 0, 2, 4 \)), in steps (ii) and (iii) of section 2 can also be evaluated accurately using the quadrature formula [6–8]:
\[ \langle x_p(X) | V_k(X + R_0) | x_q(X) \rangle = \sum_{s=1}^{K} T_{ps} T_{qs} \left[ V_k(X(s) + R_0) \right], \]

(14)

where \( T = (T^K) \) is the orthogonal matrix which diagonalizes the \( X \) matrix \( (X_{ij}) \) in the harmonic oscillator basis of truncated size \( K \), and \( X(s) \) is the corresponding \( s \)th eigenvalue.

With this three-step procedure we have performed the predissociation lifetime calculations for the Ar...N\(_2\) potential shown in fig. 1. Sufficient number of inner basis function (say \( K \)) must be included in the step (ii) to ensure the proper convergence of potential matrix elements. In the case of Ar...N\(_2\) system, we found the choice of \( K \geq N + 20 \) is adequate for high-precision calculations. Shown in fig. 4 is a typical example of the resonance \( \alpha \) trajectory for the case of six coupled channels \( (l = 0, 2, 4, 6, 8, 10, J = M = 0) \) with \( N = 30 \) for each channel and \( K = 60 \). The desired resonance position is clearly identified by the sharp kink point in the diagram. (Since the complex symmetric matrix (cf. fig. 3) is of 180 X 180 in dimension (for the six-channel case), we adopted the more efficient inverse iteration procedure [18] which solves one desired complex eigenvalue at one time.) In table 2, the convergence of the resonance position of a typical Ar...N\(_2\) metastable state is shown with respect to the number of coupled channels. We note that it is essential to include all open channels and at least two closed channels to get fully converged results. Finally in table 3 we summarize the converged results (seven-channel calculations) for the several resonance energies and widths associated with the \( [\text{Ar...N}_2(l = 8)] J = M = 0 \) van der Waals molecules where \( v \) denotes the vibrational quantum number of the van der Waals bond. Also shown in table 3 are the results of Beswick and Requena [12] who made similar calculations of the rotational predissociation of Ar...N\(_2\) system based on the following approximations: (a) The numerical potentials of Lee and Kim [9] were fitted in approximate analytic Morse forms so that the bound and continuum wavefunctions can be computed analytically. (b) Simple “golden-rule” treatment was used to compute the predissociation resonance energies and widths. (c) Only open channels were included and continuum—continuum couplings were ignored. Comparison of the golden-rule and the more accurate current CCCC results indicates substantial differences in both \( E_R \) and \( \Gamma \). However, the golden-rule approximation appears to be useful for qualitative prediction of predissociation resonance energies.

### Table 2

<table>
<thead>
<tr>
<th>( N_c )</th>
<th>Open channels (^a)</th>
<th>Closed channels (^a)</th>
<th>( E_R ) (cm(^{-1}))</th>
<th>( \Gamma/2 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>(4, 6)</td>
<td>(8, 10)</td>
<td>109.33</td>
<td>2.36</td>
</tr>
<tr>
<td>5</td>
<td>(2, 4, 6)</td>
<td>(8, 10)</td>
<td>105.72</td>
<td>3.08</td>
</tr>
<tr>
<td>5</td>
<td>(0, 2, 4, 6)</td>
<td>(8)</td>
<td>107.84</td>
<td>1.51</td>
</tr>
<tr>
<td>6</td>
<td>(0, 2, 4, 6)</td>
<td>(8, 10)</td>
<td>106.50</td>
<td>2.80</td>
</tr>
<tr>
<td>7</td>
<td>(0, 2, 4, 6)</td>
<td>(8, 10, 12, 14)</td>
<td>106.50</td>
<td>2.90</td>
</tr>
<tr>
<td>8</td>
<td>(0, 2, 4, 6)</td>
<td>(8, 10, 12, 14)</td>
<td>106.50</td>
<td>2.90</td>
</tr>
</tbody>
</table>

\(^a\) The numbers shown are the channel quantum number \( j \) (or \( l \)) values.
Table 3
Summary of the converged resonance energies ($E_R$) and widths ($W$) of rotationally predissociated metastable states of the
Ar-N$_2$ van der Waals molecule (with $l = 8, J = M = 0$) obtained in the present study (7 coupled channels $l = 0, 2, 4, 6, 8, 10, 12$). All the channel blocks have the same basis size $N_r = 30$. Shown also here are the results obtained in ref. [12] using approximate analytic potentials and simple golden-rule approximation.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$l$</th>
<th>CCCC b)</th>
<th>Golden rule c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_R$ (cm$^{-1}$)</td>
<td>$W$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>79.74</td>
<td>3.28</td>
</tr>
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<td></td>
<td>106.50</td>
<td>5.80</td>
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<td>2</td>
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<td>125.64</td>
<td>4.84</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>137.58</td>
<td>3.28</td>
</tr>
</tbody>
</table>

a) Stretching vibrational quantum number of the van der Waals bond. Only four metastable states can be determined with high precision with 30 HO basis.
b) Present complex-coordinate coupled-channel results
c) Ref. [12]

In conclusion, we have presented in this paper a stable computational procedure and demonstrated for the first time that the method of complex scaling transformation can be extended with high precision to systems involving only numerical potential information.

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