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Resonances of triatomic van der Waals molecules by the complex discrete variable representation*

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Summary. The results of Light and co-workers [J. Chem. Phys. 85:4594 (1986); 86:3065 (1987); 92:2129 (1990)] for the Hamiltonian matrix of a triatomic van der Waals molecule in the discrete variable representation, DVR, is extended to complex-scaled Hamiltonians. As an illustrative numerical example the $J = 1$ resonances positions and widths of a van der Waals model system were obtained by the calculation of the complex-scaled Hamiltonian matrix in the DVR formalism.

Key words: Discrete variable representation (DVR) – Complex-scaled Hamiltonian matrix – Triatomic van der Waals molecules

1. Introduction

It is now becoming routine to calculate bound rotation-vibration states of triatomic molecules from first principles, and computer programs have been developed by Sutcliffe, Tennyson, and co-workers [1, 2].

Taking into account rotational symmetry, the problem reduces to one involving three internal variables. For an atom-diatom triatomic van der Waals molecule, these are conveniently taken to be: r, the diatomic bond length; R, the distance from the atom to the center of mass of the diatomic; and θ, the angle between the diatomic bond and the van der Waals bond.

The rotation-vibration energy levels are then determined by the masses of the atoms and the potential energy function $V(R, r, \theta)$. Often, this function is computed by quantum chemistry techniques, and is known at only fixed values of θ. Bačic and Light have developed a technique – called the discrete variable representation (DVR) – which is well suited to this situation [3].

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Tennyson and Henderson have recently treated $J = 0$ and $J = 1$ states of H_3^+ using the DVR approach [4]. Their derivation is well suited for incorporation in existing computer programs for triatomic molecules. More recently Choi and Light determined the bound and quasibound states up to $J = 60$ of Ar-HCl van der Waals complex by the DVR approach [5]. They obtained the resonance widths by calculating the expectation value of the Miller–Schwartz–Tromp [6] outgoing symmetrized flux operator. Another recent application of the DVR method is by Mlidenovic and Bačic to the floppy HCN/HNC molecule [7].

The purpose of this work is to show that the DVR approach can be directly applied to the calculation of resonance states through the use of complex-scaled Hamiltonians [10–13]. The resonance positions and widths are associated with complex eigenvalues of the DVR transformed Hamiltonian matrix and there is no need to calculate the quasi-bound eigenvectors. In Sects. 2 and 4 we show that by complex scaling of the dissociative coordinate only and by using a *real* basis set in the solution of the adiabatic Hamiltonians, the DVR transformed Hamiltonian matrix has a complex symmetric form. As an illustrative numerical example we chose a well-worked problem which has been used before as a testbed for new theories and computational methods.

2. The complex wave equation

In order to determine the resonance positions and widths R is taken as the complex scaled coordinate, $R = R' \exp(i\beta)$ where $R' \in [0, \infty]$ and the non-dissociative coordinates θ and r remain unscaled.

We adopt a body-fixed coordinate system, as described in the introduction. We specify that the body-fixed z-axis coincides with the van der Waals bond, and that the diatomic lies in the body-fixed xz-plane. With these coordinates, stationary state eigenfunctions of the total angular momentum (quantum numbers, J, M) have the form:

$$\Psi = \sum_{\Omega=-J}^{J} \chi_\Omega(R, r, \theta) D^J_{\Omega M}(\alpha\beta\gamma) \tag{1}$$

where $D^J_{\Omega M}$ is a representation coefficient of the rotation from space-fixed to body-fixed coordinates, and α, β, γ are the Euler angles specifying the transformation.

The internal wavefunctions χ_Ω satisfy a set of coupled equations:

$$\begin{aligned}\left\{\frac{\hat{P}_R^2}{2\mu} + \frac{J(J+1) + \hat{j}^2 - 2\Omega^2}{2\mu R^2} + \frac{\hat{P}_r^2}{2\mu_d} + \frac{\hat{j}^2(\Omega)}{2\mu_d r^2} + \hat{V}_d(r) + \hat{V}(R, r, \theta) - E\right\} \chi_\Omega(R, r, \theta) \\ = \frac{\lambda_+(J, \Omega)\hat{j}_-(\Omega)}{2\mu R^2}\chi_{\Omega+1} + \frac{\lambda_-(J, \Omega)\hat{j}_+(\Omega)}{2\mu R^2}\chi_{\Omega-1}\end{aligned} \tag{2}$$

In these equations, $\hat{V}_d(r)$ is the diatomic potential energy; Ω is the quantum number of $\hat{J}_z$ and $\hat{j}_z$; and $\hat{j}^2(\Omega), \hat{j}_\pm(\Omega)$ are the diatomic angular momentum operators. Also:

$$\lambda_\pm(J, \Omega) = [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \tag{3}$$

The natural basis for representing the θ-dependence of the χ_Ω is the set of associated Legendre polynomials, which satisfy

$$\begin{aligned}\hat{j}^2 P_j^\Omega &= j(j+1) P_j^\Omega \\ \hat{j}_\pm P_j^\Omega &= \lambda_\pm(J, \Omega) P_j^{\Omega\pm1}\end{aligned} \tag{4}$$

Hence:

$$\chi_\Omega(R, r, \theta) = \sum_{j=\Omega} P_j^\Omega(\theta)\chi_{j\Omega}(R, r), \quad j = \Omega, \Omega + 1, \ldots \tag{5}$$

Substituting this expansion into Eq. (2) and using the parity relation:

$$\chi_\Omega(R, r, \theta) = p(-)^J \chi_{-\Omega}(R, r, \theta), \quad p = \pm 1 \tag{6}$$

results in an expanded set of coupled equations [8, 9].

$$\begin{aligned} &\left\{\frac{\hat{P}_R^2}{2\mu} + \frac{J(J+1) + j(j+1) - 2\Omega^2}{2\mu R^2} + \frac{\hat{P}_r^2}{2\mu_d} + \frac{j(j+1)}{2\mu_d r^2} + \hat{V}_d(r) - E\right\}\chi_{j\Omega} \\ &\quad + \sum_{j'=\Omega} \langle j\Omega|\hat{V}|j'\Omega\rangle \chi_{j'\Omega} \\ &\quad = f_+ \frac{\lambda_+(J, \Omega)\lambda_+(j, \Omega)}{2\mu R^2}\chi_{j,\Omega+1} + f_- \frac{\lambda_-(J, \Omega)\lambda_-(j, \Omega)}{2\mu R^2}\chi_{j,\Omega-1} \end{aligned} \tag{7}$$

where

$$f_\pm = [1 + p(-)^J(\delta_{\Omega 0} + \delta_{\Omega \pm 1,0})]^{1/2} \tag{8}$$

In these equations, Ω takes on only non-negative values greater than $\bar{\Omega}$, where: $\bar{\Omega} = [1 - p(-)^J]/2$. Also:

$$\langle j\Omega|\hat{V}|j'\Omega\rangle = \int P_j^\Omega(\theta)\hat{V}(R, r, \theta)P_{j'}^\Omega(\theta)\, d\tau_\theta \tag{9}$$

For compactness of notation, it is convenient to write Eq. (7) in a matrix notation:

$$(H - E1)\chi = 0 \tag{10}$$

where H is a partitioned matrix of operators:

$$H = \begin{bmatrix} H_{\bar{\Omega}} - E1 & -\lambda_{\bar{\Omega},\bar{\Omega}+1} & 0 & \cdots \\ -\lambda^\dagger_{\bar{\Omega},\bar{\Omega}+1} & H_{\bar{\Omega}+1} - E1 & -\lambda_{\bar{\Omega}+1,\bar{\Omega}+2} & \cdots \\ 0 & -\lambda^\dagger_{\bar{\Omega}+1,\bar{\Omega}+2} & H_{\bar{\Omega}+2} - E1 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{11}$$

and χ is a partitioned vector:

$$\chi = \begin{bmatrix} \chi_{\bar{\Omega}} \\ \chi_{\bar{\Omega}+1} \\ \chi_{\bar{\Omega}+2} \\ \vdots \end{bmatrix} \tag{12}$$

The diagonal matrices H_Ω contain only diagonal elements except for the matrix of $V(R, r, \theta)$. The off-diagonal matrices $\lambda_{\Omega,\Omega+1}$ are matrices in which only the elements on the diagonl lying below the main diagonal have non zero values. As a result of the complex scaling the Hamiltonian matrix $\hat{H}$ given in Eq. (11) has a complex symmetric form.

3. The DVR transformation of the complex symmetric Hamiltonian matrix

Following Bačic and Light [3], we define a non-square DVR transformation matrix T^Ω with elements:

$$T^{\Omega}_{j\alpha} = \omega^{1/2}_{\alpha} P^{\Omega}_{j}(\theta_{\alpha}) \quad \alpha = 1, 2, \ldots, N_{\alpha}; j = \Omega, \Omega + 1, \ldots, N_{\alpha} + \Omega \tag{13}$$

where θ_α and ω_α are respectively the points and weights of a N_α-point Gaussian quadrature. The points and weights depend upon Ω, but we shall not reflect this in the notation (the definition of the quadrature points of $\Omega > 0$ is given in Sect. 4). Because of the properties of orthogonal polynomials:

$$T^{\Omega\dagger} T^{\Omega} = T^{\Omega} T^{\Omega\dagger} = 1 \tag{14}$$

From the T^{Ω} we form a partitioned transformation matrix T with diagonal elements T^{Ω}, and use it to transform Eq. (10):

$$T^{\dagger}(H - E1)T(T^{\dagger}\chi) = 0 \tag{15}$$

or

$$(\bar{H} - E1)\bar{\chi} = 0$$

The advantage of this transformation is that it brings the matrix of $V(R, r, \theta)$ into diagonal form. Let us examine this step in detail:

$$(T^{\Omega\dagger} V T^{\Omega})_{\alpha'\alpha} = \sum_{j'} \sum_{j} T^{\Omega}_{j'\alpha'} \langle j'\Omega | V | j\Omega \rangle T^{\Omega}_{j\alpha} \tag{16}$$

The rule for numerical quadrature is, however:

$$\begin{aligned} \langle j'\Omega | V | j\Omega \rangle &\cong \sum_{\alpha''} P^{\Omega}_{j'}(\theta_{\alpha''}) V(R, r, \theta_{\alpha''}) P^{\Omega}_{j}(\theta_{\alpha''}) \omega_{\alpha''} \\ &= \sum_{\alpha''} T^{\Omega}_{j'\alpha''} T^{\Omega}_{j\alpha''} V(R, r, \theta_{\alpha''}) \end{aligned} \tag{17}$$

Substituting Eq. (17) into Eq. (16), and making use of Eq. (14) gives:

$$(T^{\Omega\dagger} V T^{\Omega})_{\alpha'\alpha} = V(R, r, \theta_{\alpha}) \delta_{\alpha'\alpha} \tag{18}$$

The disadvantage of the DVR transformation is that any term in H involving $\hat{j}$ becomes nondiagonal. Thus we define $\bar{L}_{\Omega}$ with elements.

$$\bar{L}_{\alpha'\alpha\Omega} = \left[\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2} \right] \sum_{j=\Omega}^{N_\alpha + \Omega} j(j + 1) T^{\Omega}_{j\alpha'} T^{\Omega}_{j\alpha} \tag{19}$$

and $\bar{L}_{\Omega,\Omega+1}$ with elements:

$$\bar{L}_{\alpha',\alpha,\Omega,\Omega+1} = -f_{+} \frac{\lambda_{+}(J, \Omega)}{2\mu R^2} \sum_{j=\Omega+1}^{N_\alpha + \Omega} \lambda_{+}(j, \Omega) T^{\Omega}_{j\alpha'} T^{\Omega+1}_{j\alpha} \tag{20}$$

Then, the matrix $\bar{H}$ has the partitioned form:

$$\begin{bmatrix} \bar{H}_{\Omega} - E1 & \bar{L}_{\Omega,\Omega+1} & 0 & \cdots \\ (\bar{L}_{\Omega,\Omega+1})^{\dagger} & \bar{H}_{\Omega+1} - E1 & \bar{L}_{\Omega+1,\Omega+2} & \cdots \\ 0 & (\bar{L}_{\Omega+1,\Omega+2})^{\dagger} & \bar{H}_{\Omega+2} - E1 & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{21}$$

where the diagonal blocks have the structure:

$$\bar{H}_{\Omega} = \bar{H}^{diag}_{\Omega} + \bar{L}_{\Omega} \tag{22}$$

and

$$\bar{H}^{diag}_{\Omega} = \frac{\hat{P}^2_R}{2\mu} + \frac{\hat{P}^2_r}{2\mu_d} + \frac{J(J + 1) - 2\Omega^2}{2\mu R^2} + \hat{V}_d(r) + \hat{V}(R, r, \theta_{\alpha}) \tag{23}$$

Except for the approximation made in Eq. (17), Eq. (15), with elements defined in Eqs. (19–23), is equivalent to the original set of coupled equations, Eq. (10). The eigenvector $\bar{\chi}$ is still blocked according to Ω, but within each block has elements labelled by α. The eigenvector χ is obtained by transformation:

$$\chi = T\bar{\chi} \tag{24}$$

In Eq. (23), since θ_α depends on Ω, it might be presumed that the potential V would need be evaluated at all of the Gaussian points. It is consistent with the approximation made in Eq. (17) to evaluate V at the points for $\Omega = 0$, and use polynomial interpolation to evaluate V at the points for $\Omega > 0$. So far the use of complex scaled coordinate R has not introduced any complication, apart from the requirement that $\hat{V}$ be dilation analytic in R' (even this requirement can be avoided by using the exterior scaling procedure).

4. The finite basis set approximation

The coupled equations represented by Eq. (15) may be solved approximately by expanding $\bar{\chi}$ in a basis of product functions depending on R and r. We choose eigenfunctions of the adiabatic Hamiltonian:

$$\left\{\frac{\hat{P}_R^2}{2\mu} + \frac{\hat{P}_r^2}{2\mu_d} + \hat{V}_d(r) + \hat{V}(R, r, \theta_\alpha) - \epsilon_k(\theta_\alpha)\right\} \phi_{k\alpha}(R, r) = 0 \tag{25}$$

Note that when R is complex scaled ϵ_k and $\phi_{k\alpha}$ are complex too (for bound states ϵ_k are real). The complex $\phi_{k\alpha}$ are obtained at α's for $\Omega = \bar{\Omega}, \bar{\Omega} + 1, \ldots$. The procedure by which the quadrature points for different Ω values are obtained is described in Sect. 4 (see Eqs. (36–37)).

This basis is independent of J and Ω, and can be used to expand the elements of $\bar{\chi}$:

$$\bar{\chi}_{\alpha\Omega} = \sum \phi_{k\alpha}(R, r) C_{k\alpha\Omega} \tag{26}$$

The coefficients $C_{k\alpha\Omega}$ and the rotation-vibration energies E are then obtained as eigenvalues of

$$(\bar{\bar{H}} - E1)C = 0$$

where

$$\bar{\bar{H}} = \begin{bmatrix} H_{\bar{\Omega}} - E1 & L_{\bar{\Omega},\Omega+1} & 0 & \ldots \\ (L_{\bar{\Omega},\Omega+1})^\dagger & H_{\bar{\Omega}+1} - E1 & L_{\bar{\Omega}+1,\Omega+2} & \ldots \\ 0 & (L_{\bar{\Omega}+1,\bar{\Omega}+2})^\dagger & H_{\Omega+2} - E1 & \ldots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{27}$$

where

$$\begin{aligned} \bar{\bar{H}}_{\alpha'k',\alpha k\Omega} = {} & \epsilon_k(\theta_\alpha)\lambda_{\alpha'\alpha}\lambda_{k'k} \\ & + \frac{J(J+1) - 2\Omega^2}{2\mu} \langle\phi_{k'\alpha}| \frac{1}{R^2} |\phi_{k\alpha}\rangle\lambda_{\alpha'\alpha} \\ & + \langle\phi_{k'\alpha'}|\bar{L}_{\alpha'\alpha\Omega}|\phi_{k\alpha}\rangle \end{aligned} \tag{28}$$

and

$$\bar{\bar{H}}_{\alpha' k',\alpha k,\Omega'\Omega} = \langle \phi_{k'\alpha'} | \bar{L}_{\alpha'\alpha\Omega'\Omega} | \phi_{k\alpha} \rangle \tag{29}$$

Making use of Eqs. (19) and (20), we have:

$$\langle \phi_{k'\alpha'} | \bar{L}_{\alpha'\alpha\Omega} | \phi_{k\alpha} \rangle = \sum_{j=\Omega}^{N_\alpha+\Omega} j(j+1) T^{\Omega}_{j\alpha'} T^{\Omega}_{j\alpha} \langle \phi_{k'\alpha'} | \frac{1}{2\mu R^2} + \frac{1}{2\mu r^2} | \phi_{k\alpha} \rangle \tag{30}$$

and

$$\langle \phi_{k'\alpha'} | \bar{L}_{\alpha'\alpha\Omega'\Omega} | \phi_{k\alpha} \rangle = -f_{+} \lambda_{+}(J, \Omega) \sum_{j=\Omega+1}^{N_\alpha+\Omega} \lambda_{+}(j, \Omega) T^{\Omega}_{j\alpha'} T^{\Omega+1}_{j\alpha} \langle \phi_{k'\alpha'} | \frac{1}{2\mu R^2} | \phi_{k\alpha} \rangle \tag{31}$$

Thus, we see that, after solving for the eigensolutions $\{\epsilon_k(\theta_\alpha), \phi\}$, we need only compute the matrices of R^{-2} and r^{-2} and diagonalize the matrix H to obtain the rotation-vibration energies and wavefunctions.

5. Illustrative numerical example – Resonance positions and matrix by the complex scaled DVR

Resonance positions and widths are obtained by performing an analytical continuation [10–13] of the DVR formalism as has been shown in Sects. 3–4.

By scaling the reaction coordinate into the complex plane according to:

$$R' \rightarrow R' e^{i\beta} \equiv R \tag{32}$$

we obtain a complex symmetric Hamiltonian matrix. This matrix's complex eigenvalues give the resonance positions (real part of the eigenvalue), and widths (imaginary part of the eigenvalue), provided that they are stable with respect to variation of the scaling angle β.

We tested our method on a model potential proposed by Levine, Johnson, Muckerman, and Bernstein [15]. The potential describes the interaction of structureless atom weakly bound to diatomic rigid rotor.

The Hamiltonian of the system is given by:

$$\hat{H}(R, \theta) = \frac{1}{2\mu}\left[-\hbar^2 \frac{\partial^2}{\partial R^2} + \frac{\hat{l}^2(R)}{R^2}\right] + B_{rot}\hat{j}^2(r) + V(R, \theta)$$

where

$$V(R, \theta) = V_0(R) + V_2(R) P_2(\cos\theta)$$
$$V_0(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$
$$V_2(R) = 0.6\epsilon\left(\frac{\sigma}{R}\right)^{12} \tag{33}$$

with the parameters

$$\delta = 3.0\,\text{Å} \qquad \epsilon = 384.092\ \text{cm}^{-1}$$
$$B_{rot} = 60.962\ \text{cm}^{-1} \qquad \mu = 1.34015\ \text{a.u.} \tag{34}$$

The $J = 0$ resonances of this system were investigated using the Complex Coordinate Method (CCM) by various authors [14, 16–19]. The $J = 1$ even parity states were investigated by Chu [17].

We applied the DVR procedure described in Sects. 1–3, using 30 harmonic oscillator basis functions with frequency $\omega = 1$ in order to describe the spatial coordinate, and dissecting the angular coordinate into $N_\alpha = 7$ quadrature angles.

The quadrature angles are Ω-dependent, and were obtained as the eigenvalues of a matrix A:

$$A_{jj'} = \langle P_j^\Omega(\theta) | \cos\theta | P_{j'}^\Omega(\theta) \rangle = \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & 1 & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & 1 & j' \\ \Omega & 0 & \Omega \end{pmatrix} \quad (35)$$

The eigenvectors of the A matrix give the quadrature weights, multiplied by the appropriate polynomial:

$$T_{j\alpha}^\Omega = \sqrt{w_\alpha} P_j^\Omega(\cos\theta_\alpha) \quad (36)$$

The main advantage of this approach is that it prevents the need to calculate directly the value of the associated Legendre polynomials at the quadrature points.

The transformation vectors, $T_{j\alpha}^\Omega$, are all we need in the subsequent calculations.

6. Results

Converged results for the $J = 0$ and the $J = 1$ resonances are presented in Tables 1 and 2, respectively.

For $J = 0$, the converged value was arrived at with a scaling angle of $\beta = 0.30$ (see Fig. 1). For $J = 1$ the resonances at positions 104.14 and 118.05 converged at $\beta = 0.28$ and $\beta = 0.31$, respectively (see Figs. 2, 3).

As can be seen from Tables 1 and 2, our results slightly differ from results previously obtained for this system. This might be due to the fact that in Refs. [14, 17 and 19] the wavefunction was expanded as a sum of only two (even) j-states, $j = 0$ and $j = 2$, whereas, in our calculation, 7 quadrature points, corresponding to $j = 0, 6$ were used.

The convergence of the resonance of $J = 0$, with respect to the number of quadrature points, is shown in Table 3. It is indeed evident from Table 3, that if we use 4 quadrature points, corresponding to $j = 0, 1, 2, 3$, the result obtained is very similar to the values of Refs. [14, 17 and 19]. Only the inclusion of an

Table 1. Comparison of resonance energies and widths for $J = 0$ by various methods

Method	E_R (cm^{-1})	Γ (cm^{-1})
SFCCCC[a]	114.47	1.79
BFCCCC[b]	114.47	1.79
CC[c]	114	2.09
CCM[d]	114.53	2.03
This work-complex DVR	114.05	2.03
This work-CCM[e]	114.05	2.03

[a] Space fixed complex coordinate coupled channel method, Ref. [14]

[b] Body fixed complex coordinate coupled channel method Ref. [16]

[c] Numerical solution of coupled equations Ref. [15]

[d] Space fixed complex coordinate method, Ref. [19] with P_0 and P_2 as the radial basis set

[e] Same as d, but with P_0, P_2 and P_4 as the radial basis set

Table 2. Comparison of the complex resonance energies for $J = 1$ by various methods

Method	$J = 1$ 1st resonance energy	$J = 1$ 2nd resonance energy
BFCCCC[a]	$103.041 - 0.233i$	$120.065 - 0.758i$
BFCCCC CD[b]	—	$116.525 - 0.966i$
This work	$104.14 - 0.16i$	$118.05 - 0.84i$

[a] Body fixed complex coordinate coupled channel method, Ref. [16]

[b] Body fixed complex coordinate coupled channel method, with centrifugal decoupling approximation, Ref. [16]

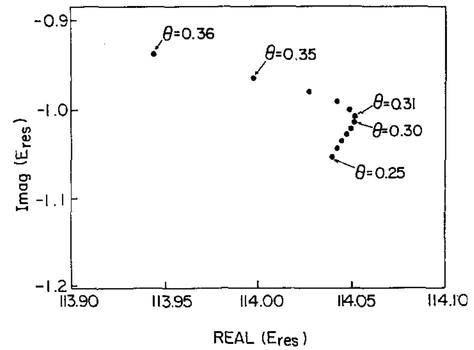
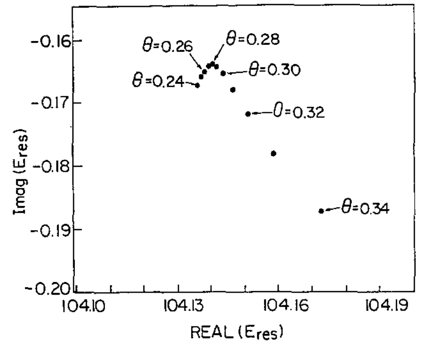
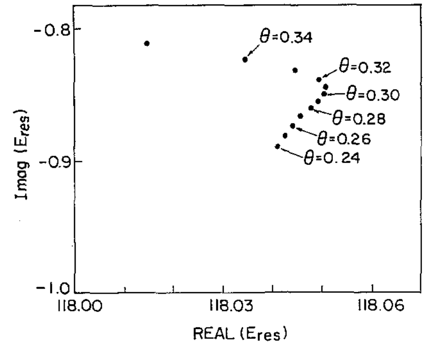


Fig. 1. β-Trajectory calculations for the rotational predissociation resonance of the triatomic van der Waals model at $J = 0$. 30 harmonic oscillator basis functions were used for the spatial coordinate. A grid of 7 angles was used to express the radial coordinate. In the graph, the symbol θ is used instead of β





Figs. 2, 3. β-Trajectory calculations for the rotational predissociation resonances of the triatomic van der Waals model at $J = 1$. In the graph, the symbol θ is used instead of β

Table 3. Convergence of the complex resonance energy of $J = 0$ with respect to the number of qaudrature points – N_α

N_α	$J = 0$ Resonance energy
3	$103.95 - 36.134i$
4	$114.52 - 0.991i$
5	$114.03 - 1.016i$
6	$114.05 - 1.015i$
7	$114.05 - 1.015i$

additional even j-state, $j = 4$, alters this result. We also repeated the calculations of Ref. [19] for the resonance at $J = 0$, adding P_4 to the radial basis set. The result, also presented in Table 1, was identical to the result obtained with DVR.

It is not possible to use a very small number of points of the DVR calculation, since the method is based on the expansion of the unity operator in (associated) Legendre polynomials (Eq. (14)). The method is, therefore, especially suited to problems with strong coupling between different j-states, where we anyway cannot truncate the expansion of the wavefunction in (associated) Legendre polynomials after a small number of terms.

7. Conclusions

To obtain rotation-vibration wavefunctions, bound states and resonance energies the following steps are required:

1. Solve Eq. (25) to obtain $\{\epsilon_k(\theta_\alpha), \phi_{k\alpha}(R, r)\}$. R is complex scaled by the factor $\exp(i\beta)$. The quadrature points of $\Omega \neq 0$ are defined in Eqs. (36–37). In order to get complex symmetric Hamiltonian matrices real basis functions to expand $\phi_{k\alpha}$ should be used.

2. Construct the matrices of R^{-2} and r^{-2} in the basis $\phi_{k\alpha}$.

3. Construct the complex symmetric matrix $\bar{\bar{H}}$ (Eq. (27)) according to Eqs. (28–31).

4. Diagonalize $\bar{\bar{H}}$ and obtain the eigenvectors C and energies E.

5. Construct the internal wavefunctions χ_Ω, using the transformations given by Eqs. (26), (24) and (5).

$$\chi_{j\Omega}(R, r) = \sum_\alpha T^\Omega_{j\alpha} \bar{\chi}_{\alpha\Omega} = \sum_\alpha \sum_k T^\Omega_{j\alpha} C_{k\alpha\Omega} \phi_{k\alpha}(R, r) \tag{37}$$

and

$$\chi_\Omega(R, r, \theta) = \sum_{j=\Omega} P^\Omega_j(\theta) \chi_{j\Omega}(R, r), \quad \Omega \geqslant 0 \tag{38}$$

with

$$\chi_\Omega(R, r, \theta) = p(-)^J \chi_{-\Omega}(R, r, \theta) \tag{39}$$

The formalism presented here results in a complex symmetric Hamiltonian matrix. In such a case the expectation valve of any given operator $\hat{O}$ is defined by:

$$\int \chi_\Omega(R, r\theta)\hat{O}\chi_\Omega(R, r, \theta)\, dR\, dr\, d\tau_\theta \tag{40}$$

(i.e., $\langle \chi_\Omega^* | \hat{O} | \chi_\Omega \rangle$) and *not* by the conventional scalar product $\langle \chi_\Omega | \hat{O} | \chi_\Omega \rangle$). However, it is not hard to apply the DVR approach to complex scaled Hamiltonians when complex basis functions are used. In such a case the Hamiltonian matrix will not have a complex symmetric form and expectation values or transition amplitude matrix elements should be calculated with some further caution. The right eigenfunctions are obtained by the diagonalization of the Hamiltonian matrix H (Eq. (27)) as described in the text. The left eigenfunctions, however, are obtained by the diagonalization of the transposed matrix H^t (see the discussion on c-inner product in Ref. [20]). The numerical study given in Sect. 5 illustrates the applicability of the complex DVR procedure in calculating resonance positions and widths. The use of the DVR approach in calculating resonance positions and widths of more realistic systems is now under process.

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