BODY-FIXED COMPLEX-COORDINATE COUPLED-CHANNEL FORMALISM
FOR ROTATIONAL PREDISSOCIATION OF VAN DER WAALS MOLECULES

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The method of complex-coordinate coupled-channel (CCCC) formalism previously developed in the space-fixed (SF) frame is reformulated in the body-fixed (BF) frame, more appropriate for strong-coupling van der Waals complexes. The utility of the method is demonstrated through a study of the level widths and energies of rotationally predissociating atom-diatom model systems. The possible usefulness of incorporating the centrifugal decoupling approximation in the BF CCCC theory is pointed out.

1. Introduction

There is currently much interest in the study of spectroscopy, structure and predissociation dynamics of weakly bound van der Waals molecules [1,2]. In this paper we are concerned with the accurate prediction of resonance energies and widths (intrinsic lifetimes) of metastable states of van der Waals molecules. Such information, besides providing useful additional information on well depths and anisotropy of the intermolecular interactions, is important to the elucidation of the general features of bond-breaking processes in chemical systems where the predissociation occurs by converting the internal vibration—rotation energies of the complexes into relative kinetic energies of the fragments. In addition, a knowledge of the lifetimes of such levels is relevant to the detectability of the complexes by supersonic beam experiments and to the feasibility of isotope separation using the technique of photoinduced predissociation of selectively excited van der Waals molecules [3].

Previous theoretical works of this problem have been summarized by Beswick and Jortner [2]. Recently a complex-coordinate coupled-channel (CCCC) formalism in space-fixed (SF) coordinates, employing only $L^2$ (square integrable) basis functions and the use of complex-coordinate transformation [4,5], has been proposed [6,7]. Besides its practical simplicity in that only bound-state functions are involved and no asymptotic boundary conditions need to be enforced, the method is also readily extendable to many-channel problems involving multiple coupling continua [8,9].

In the present work we focus on the alternative formulation of the CCCC theory in the body-fixed (BF) frame of coordinates. The situation here is similar to the well-known quantum theory of molecular scattering which can be formulated either in SF [10] or in BF [11] coordinates. Although the two formulations are equivalent, the SF theory appears more appropriate for weak-coupling complexes and the BF theory more natural for strong-coupling complexes [1,2]. Thus a development of BF CCCC formalism is desirable. In addition, for van der Waals complexes which are only slightly asymmetric tops such as Ar—HCl [12], the “tumbling” angular momentum quantum number $\Omega$ (see discussion in section 2) in the BF frame is nearly conserved, and the centrifugal decoupling approximation [13] may be effective. This drastically reduces the number of coupled channels and provides a tremendous simplification and computational advantage in the BF frame. In section 2 the BF CCCC formalism is briefly outlined. In section 3, we illustrate the method by a study of rotational predi-
association of two model atom–diatom complexes involving medium and strong anisotropies respectively. Extension of the method to vibrational predissociation is straightforward and will be discussed elsewhere.

2. Complex-coordinate coupled-channel formulation in body-fixed frame

The theory of atom–diatom van der Waals molecules may be formulated using either space-fixed or body-fixed coordinates. The coordinates and axis systems are shown in fig. 1. The primed axes refer to a space-fixed (SF) coordinate system while the unprimed axes refer to the body-fixed (BF) coordinate system. The BF axes \( \{x',y',z'\} \) are defined such that \( z' \) is parallel to \( \mathbf{R} \), the vector of length \( R \) running from the diatom centre-of-mass to the atom, and \( y' \) lies in the \( \{R,r\} \) plane, where \( r \) is the diatom internuclear vector. In the SF frame, the dynamics of the system are described by \( R \), \( r \), and the polar angles specifying the orientation of \( \mathbf{R} \) and \( r \). In the BF frame, the relevant coordinates are \( R \), \( r \), \( \theta \) (= \( \cos^{-1} \left( \mathbf{R} \cdot \mathbf{R} \right) \)), and the three Euler angles defining the orientation of \( \{x,y,z\} \) relative to \( \{x',y',z'\} \).

The Hamiltonian of a triatomic van der Waals molecule \( \text{A} \ldots \text{BC} \), where \( \text{A} \) is a structureless atom and \( \text{BC} \) a diatomic rigid rotor (with \( r = r_0 \)), may be written in the SF frame as [6,8]

\[
H(R, \theta) = \left\langle \frac{1}{2\mu} \right\rangle \left\{ -\hbar^2 \partial^2 / \partial R^2 + \mu \frac{\partial^2}{\partial \theta^2} \right\} + B_{\text{rot}} j^2(R) + V(R, \theta).
\]

In this equation \( \mu = m_A (m_B + m_C) / (m_A + m_B + m_C) \), \( \cos \theta = \mathbf{R} \cdot \mathbf{R} \), \( B_{\text{rot}} \) is the rotational constant of the diatom, \( j \) is the rotational angular momentum of BC, \( I \) is the orbital angular momentum of BC and \( \text{A} \) about each other, \( V(R, \theta) \) is the interaction potential of \( \text{A} \) and BC, and \( J = j + I \) is the total angular momentum.

In the BF frame, the Hamiltonian is identical to (1) except that \( R \) and \( r \) are expressed relative to the unprimed axes and the angular momentum operator for the rotation of \( R \) (i.e. \( \mathbf{I} \)) is written as the difference between the total angular momentum \( J \) and that associated with the rotation of \( \mathbf{R} \) (i.e. \( \mathbf{I} \)), yielding

\[
H(R, \theta) = \left\langle \frac{1}{2\mu} \right\rangle \left\{ -\hbar^2 \partial^2 / \partial R^2 + (J - j)^2 / R^2 \right\} + B_{\text{rot}} j^2 + V(R, \theta).
\]

In the BF frame, the projection of the rotational angular momentum \( j \) on the body-fixed \( z \) (i.e. \( \mathbf{R} \)) is denoted by the “tumbling” angular momentum quantum number \( \Omega \), so that the eigenfunctions of \( j^2 \) are \( Y_{\Omega}(\hat{\mathbf{R}}) \). By conservation of angular momentum, the projection of the total angular momentum \( J \) on this BF \( z \) axis is also equal to \( \Omega \). As usual, the interaction potential \( V(R, \theta) \) can be expanded in terms of the Legendre polynomials \( P_\Omega(\cos \theta) \), yielding

\[
V(R, \theta) = \sum_{\Omega=0}^{\infty} V_{\Omega}(R) P_\Omega(\cos \theta).
\]

The operator \( (J - j)^2 \) in eq. (2) may be expressed as

\[
(J - j)^2 = (J^2 + j^2 - 2j_0^2) - (J_+ J_- + J_- J_+),
\]

where \( J_+ = J_x \pm iJ_y \) and \( J_- = J_x \mp iJ_y \). Making use of (4), the Hamiltonian (2) becomes

\[
H(R, \theta) = \left\{ -\hbar^2 \partial^2 / \partial R^2 + (J^2 + j^2 - 2j_0^2) / 2R^2 \right\}

+ B_{\text{rot}} j^2 + V(R, \theta) - (J_+ J_- + J_- J_+) / 2R^2.
\]

Here the coupling between different modes of van der Waals vibrational motions is induced by the anisotropic part of \( V(R, \theta) \) and by the last term in eq. (5). In the total angular momentum \( (J, M) \) representation
(where $M$ is the $z$ component of $J$ in a SF axis system),
an appropriate angular basis for wavefunction expansion in BF coordinates is
\[ \Theta_{JM}^{\Omega}(\hat{r}, \hat{\theta}) = [(2J + 1)/4\pi]^{1/2} D_{JM}^{J} (\hat{r}, \hat{\theta}) Y_{J}^{M} (\hat{\theta}), \]  
(6)
where $D_{JM}^{J}$ is the symmetric top wavefunction.

It is expedient to define a scheme for labeling of the eigenstates of the complex uniquely. In the zero-coupling limit, each isotropic state is an eigenfunction of $J^2, J_z^{SF}, J_z^{BF}$, and $J_z^{BF}$ and may be labeled by $(JM)\Omega$. The latter may be decomposed into a radial and an angular function
\[ \phi_{JM}^{\Omega}(R, \hat{r}, \hat{\theta}) = \Theta_{JM}^{\Omega}(\hat{r}, \hat{\theta}) Y_{J}^{M} (\hat{\theta}), \]  
(7)

When the coupling terms are turned on, the state will be only an eigenfunction of $J^2$ and $J_z^{SF}$. Thus only $J$ and $M$ are good quantum numbers in the perturbed state. Nevertheless, the isotropic function $(JM)\Omega$ still forms a convenient unperturbed basis for our present study.

We now discuss the complex-coordinate coupled-channel formulation in the BF frame. According to the theory of dilatation transformation [4,5], the energy ($E_R$) and the width ($\Gamma$) associated with a metastable state may be determined by the solution of the complex eigenvalue of a non-hermitean hamiltonian $H_{\phi}(R, \theta)$, obtained by applying the dilatation or complex-coordinate transformation [4], $R \rightarrow R \exp (i\alpha)$, to the real hamiltonian $H(R, \theta)$. That is,
\[ H(R, \theta) \rightarrow e^{-2i\alpha} H_{\phi}(R, \theta) \rightarrow e^{-2i\alpha} H_{\phi}(R, \theta) \]  

where $\alpha$ is the rotational angle usually taken to be a positive number. In the present study, the total wavefunction of the hamiltonian $H_{\phi}(R, \theta)$, for a given $J$ and $M$, will be expanded in terms of the complete set of the isotropic state functions $(JM)\Omega$ allowed by the symmetry. We further expand the radial function $\phi_{JM}^{\Omega}(R)$ of $(JM)\Omega$ in terms of an orthonormalized $L^2$ basis function $\{x_{\gamma}(R)\}$,
\[ \phi_{JM}^{\Omega}(R) = \sum_{n=1}^{N_{\gamma}} c_{\gamma}(R) x_{\gamma}(R), \]  
(9)

where $\gamma$ specifies the channel quantum number, $\gamma = (JM)\Omega$, $N_{\gamma}$ is the size of the truncated radial basis, and $\langle x_{\gamma'}|x_{\gamma}\rangle = \delta_{\gamma\gamma'}$. For convenience, let us define the basis function
\[ \{\gamma\Omega\} \equiv x_{\gamma}(R) \Theta_{JM}^{\Omega}(\hat{r}, \hat{\theta}), \]  
(10)
and arrange the order of the matrix elements of $H_{\phi}(R, \theta)$ in such a way that $\Omega$ is allowed to vary from 1 to $N_\gamma$ within each channel block $\gamma = (JM)\Omega$. The matrix element in the $\{\gamma\Omega\}$ representation is
\[ \langle\gamma\Omega'|H_{\phi}(R, \theta)|\gamma\Omega\rangle = e^{-2i\alpha}(\hbar^2/2\mu) \times \langle x_{\gamma'}|1 - \partial^2/\partial R^2 + (J(J+1) - \Omega^2 + 2\Omega^2/R^2)|x_{\gamma}\rangle 
\times \delta_{J\gamma}\delta_{MM'}\delta_{J\Omega}\delta_{\Omega\Omega'} 
+ B_{\text{rot}}(\partial^2/\partial R^2 + J(J+1) - \Omega^2 + 2\Omega^2/R^2) \times X_{\gamma'}(\omega, R') \]  
(11)

where
\[ d_{\gamma'}^{\gamma}(\Omega, \Omega') = (-1)^{\gamma'} \binom{(2J + 1)\gamma}{(2J + 1)\gamma'}^{1/2} \times \binom{j' k j}{-\gamma\gamma'} \]  
(12)
and
\[ \lambda_{\gamma}(\Omega, \Omega') = [J(J+1) - \Omega(\Omega + 1)]^{1/2} \times [j'(j' + 1) - \Omega(\Omega + 1)]^{1/2} 
+ [J(J+1) - \Omega(\Omega - 1)]^{1/2} \times [j(j + 1) - \Omega(\Omega - 1)]^{1/2} \]  
(13)

and ($~,~$) is the 3-j symbol. The resulting matrix of $H_{\phi}$ is a symmetric complex whose complex eigenvalues may be determined via the secular determinant
\[ \text{Det}[H_{\phi} - \gamma\Omega'|E_{\gamma}\rangle = 0. \]  
(14)

The desired metastable states are then identified by the stationary points [5-9] of the $\alpha$ trajectories of complex eigenvalues.

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3. Calculations and discussion

To assess the usefulness of the procedure outlined in section 2, we discuss below the application of this technique to the determination of resonance energies and widths of two A—BC model systems which have been considered previously by many authors using different theoretical methods [14—16]. The systems under consideration have the following potential energy form

\[ V(R, \theta) = V_0(R) + V_2(R)P_2(\cos \theta), \tag{15} \]

with

\[ V_0(R) = 4e[(a/R)^{12} - (a/R)^6], \]

and

\[ V_2(R) = 4ea(a/R)^{12}, \]

where \( a \) is the anisotropic parameter. The values of the parameters used are listed in Table 1. Both models apply to He—H\(_2\) pairs with various values for the parameters of the anisotropic part of the potential: model A represents a moderately strongly anisotropic system whereas model B a quite strongly anisotropic system.

For both systems we consider the subexcitation of A and BC such that the collision energy \( E < E_{th} \), the threshold for the first allowed rotational excitation \( (J = 0 \rightarrow 2) \). We limit the angular basis with \( j \leq 2 \) and

\[ \gamma = \min(j, J), \]

For the case \( J = 0 \), the tumbling quantum number can only take the value \( \Omega = 0 \), and the BF and SF representations are identical. For \( J \neq 0 \), strong couplings exist between different \( \Omega \) sublevels of the \( j \) manifolds. However, a partial decoupling scheme among \( \Omega \) sublevels is possible if use is made of the symmetry of the problem. Defining the even- and odd-parity wavefunctions

\[ |JM\Omega\rangle(\gamma) = 2^{-1/2}(|JM\Omega\rangle \pm |JM\Omega - 2\rangle), \quad \Omega \neq 0, \tag{16} \]

and

\[ |JM\Omega\rangle = |JM\Omega = 0\rangle, \tag{17} \]

it is easy to show that even- and odd-parity states are not coupled. In the following we shall focus our discussion on the rotational predissociation of the \( J = 0 \) and 1 even-parity metastable states.

<table>
<thead>
<tr>
<th>( J=0, n_r=0, n=0 )</th>
<th>( J=1, n_r=0, n=0 )</th>
<th>( J=2, n_r=0, n=0 )</th>
<th>( J=3, n_r=0, n=0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_r=1 )</td>
<td>( n_r=1 )</td>
<td>( n_r=1 )</td>
<td>( n_r=1 )</td>
</tr>
</tbody>
</table>

\( (n, n_r=1, 2, \ldots, N) \)

Fig 2. Matrix structure of the predissociation Hamiltonian \( H \) in the \( \gamma \gamma \) representation. Here \( \gamma = (JM\Omega) \) specifies the channel quantum number, \( n \) is the index number for the harmonic oscillator radial basis, \( n = 1, 2, \ldots, N \), \( V \) is the anisotropic potential and \( J_{l/2} \) is the centrifugal coupling term. See text for detailed explanation of the construction of appropriate coupling blocks.
The matrix of interest in the $|\gamma\rangle$ representation is shown symbolically in fig. 2. It is of a three-by-three block form for the case of $J = 1$ and of a two-by-two block form (boldly outlined) for the case of $J = 0$. Within each diagonal block specified by the channel quantum number $\gamma = (JM\Omega)$, we use the orthonormal harmonic oscillator (HO) $L^2$ basis [17]

$$\chi_n(R) = (\beta/\pi^{1/2} 2^n n!)^{1/2} H_n(\beta x) \exp\left(-\frac{1}{2} \beta^2 x^2\right)$$

(18)

to expand the bound and to discretize the continuum radial wavefunctions $\psi_{\Omega J}(R)$ defined in eq. (9). This basis set has been used recently extensively in the studies of predissociation of van der Waals molecules (using the SF CCCC theory) [6,8,9] and intense field molecular photodissociation [18]. In eq. (18), $H_n$ is a Hermite polynomial, $x = R - R_0$, and both $R_0$ and $\beta$ are adjustable parameters. The kinetic matrix elements in the HO basis can be worked out analytically and the potential matrix elements can be computed accurately using the numerical quadrature procedure devised by Harris et al. [6,19].

Using the abovementioned procedure we have performed the predissociation lifetime calculations for the $J = 0$ and 1 metastable states of models A and B. Shown in fig. 3 (fig. 4) is a typical example of the resonance $\alpha$-trajectory of the complex eigenvalue correlated with the metastable state $[J = 1, f = 2, \Omega = 0^+]$ of system A. The desired resonance positions $(E_R, -\Gamma/2)$ are clearly identified by the sharp turning points in the diagrams $[E_R = \text{Re}(E), \Gamma/2 = -\text{Im}(E)].$

In table 2, the results of the present BF CCCC calculations for the case of $J = 0$ are compared with some previous theoretical data [6,14–16]. The overall agreement appears satisfactory. We note that our BF CCCC results reproduce exactly the SF CCCC results for the special case of $J = 0$ as it should be.

![Fig. 3](image1.png)

**Fig. 3.** A typical resonance $\alpha$-trajectory (indicated by open circles) for the complex eigenvalue associated with the rotational predissociation of the metastable level $(J = 1, f = 2, |\Omega| = 0^+)$ of system A. The desired resonance position is indicated by the arrow. These are three coupled-channel calculations with $N = 30$ for each channel. Note that $\text{Re}(E) = E_R$ and $\text{Im}(E) = -\Gamma/2$.

![Fig. 4](image2.png)

**Fig. 4.** A typical resonance $\alpha$-trajectory for the metastable level $(J = 1, f = 2, |\Omega| = 1^+)$ of system A. See the caption of fig. 3 for details.
Table 2
Comparison of resonance energies and widths determined by various methods. The metastable state under consideration is correlated with the closed channel \( \Omega = 0, j = 2 \). The vibrational quantum number for the van der Waals bond stretching is 0.

<table>
<thead>
<tr>
<th>Method</th>
<th>System A</th>
<th>System B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_R ) (cm(^{-1}))</td>
<td>( \Gamma ) (cm(^{-1}))</td>
</tr>
<tr>
<td>AD a)</td>
<td>114.0 b)</td>
<td>1.80 b)</td>
</tr>
<tr>
<td>CC b)</td>
<td>114</td>
<td>2.09</td>
</tr>
<tr>
<td>SQ c)</td>
<td>114.521</td>
<td>2.146</td>
</tr>
<tr>
<td>SE d)</td>
<td>114.46</td>
<td>2.40</td>
</tr>
<tr>
<td>SF CCCC e)</td>
<td>114.47</td>
<td>1.79</td>
</tr>
<tr>
<td>BF CCCC f)</td>
<td>114.47</td>
<td>1.79</td>
</tr>
</tbody>
</table>

a) Adiabatic decoupling approximation of ref. [14]. b) Numerical solution of coupled equations of ref. [14].

c) Siegert quantization method of ref. [16]. d) Secular equation method of ref. [15].
e) Space-fixed complex-coordinate coupled-channel method of ref. [6]. Parameters used are \( R_0 = 6.3636 \, a_0 \) (Bohr radius), \( \beta = 2.0 \, a_0^{-1} \) and \( N = 20 \) for each channel.
f) Body-fixed complex-coordinate coupled-channel method; present work. Parameters used same as e).
g) Data quoted in ref. [15]. h) Uncertainty due to result being taken from a graph.

For the case \( j = 1 \), there are no previous data for comparison, and the converged resonance positions for the metastable states \( (j = 1, j = 2, \Omega = 0^* + 1^*) \) computed using the BF CCCC method (three coupled channels, cf. fig. 2) are summarized in table 3. We note that the \( (j = 2, \Omega = 1^+) \) level does not couple directly with open channel \( (j = 0, \Omega = 0^+) \) and the width of the former level is induced indirectly through the coupling between \( \Omega = 0^* \) and \( \Omega = 1^+ \) sublevels of \( j = 2 \). For system A, the splitting of the two \( \Omega \) sublevels of \( j = 2 \) is 17 cm\(^{-1}\) and the width of the \( \Omega = 1^+ \) level is as large as 30% that of the \( \Omega = 0^* \) level, indicating that the \( J_{J_{1/2}}/2\mu R^2 \) coupling term is significant here. For the (stronger anisotropic) system B, the splitting increases to 29.4 cm\(^{-1}\), whereas the width ratio \( \Gamma(\Omega = 1^+)/\Gamma(\Omega = 0^+) \) decreases to only 8.7%, suggesting that the centrifugal decoupling (CD) approximation (i.e. ignoring the \( J_{J_{1/2}}/2\mu R^2 \) coupling term) may be more effective here. Shown in table 3 are also the results of the resonance energies and widths of the metastable state \( (j = 2, \Omega = 0^+) \) using the CD approximation. These are two-channel-block (boldly outlined in fig. 2) calculations with the closed channel \( (j = 2, \Omega = 1^+) \) deleted. It is clearly seen that the CD approximation works much better for stronger anisotropic system B.

In summary, we have presented in this paper a new formulation of the complex-coordinate coupled-chan-

Table 3
Summary of the converged complex resonance energies \( (E_R, -\Gamma/2) \) of the rotationally predissociating metastable states that are correlated with the closed channels \( \Omega = 0, j = 2, \Omega = 0^* + 1^* \). The vibrational quantum number for the van der Waals bond stretching is 0.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \Omega )</th>
<th>System A b)</th>
<th>System B c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_R ) (cm(^{-1}))</td>
<td>( r/2 ) (cm(^{-1}))</td>
<td>( E_R ) (cm(^{-1}))</td>
</tr>
<tr>
<td>BF CCCC</td>
<td>0*</td>
<td>120.065</td>
<td>0.758</td>
</tr>
<tr>
<td>BF CCCC</td>
<td>1*</td>
<td>103.041</td>
<td>0.233</td>
</tr>
<tr>
<td>BF CCCC CD a)</td>
<td>0*</td>
<td>116.525</td>
<td>0.996</td>
</tr>
</tbody>
</table>

a) BF CCCC method with centrifugal decoupling (CD) approximation.
b) Parameters used are \( R_0 = 6.3636 \, a_0, \beta = 2.0 \, a_0^{-1}, \) and \( N = 30 \) for each channel.
c) Parameters used are \( R_0 = 6.50 \, a_0, \beta = 2.0 \, a_0^{-1}, \) and \( N = 30 \) for each channel.
nel theory in the body-fixed frame and demonstrated its applicability to the study of multichannel predissociation of van der Waals molecules. We have also shown the possible usefulness of the centrifugal decoupling approximation in the BF CCCC formulation which could lead to much simplification and computational advantage. We are currently applying the BF CCCC CD method to the study of the multichannel rotational predissociation of Ar–HCl complex and the details will be published elsewhere [20].

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