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Authors	Chu, Shih-I
Citation	Chu, Shih-I. "Studies of rotational predissociation of van der Waals molecule by the method of complex coordinate." The Journal of Chemical Physics 72, 4772 (1980); http://dx.doi.org/10.1063/1.439812.
DOI	10.1063/1.439812
Publisher	Elsevier
Download date	2024-07-31 05:21:16
Link to Item	http://hdl.handle.net/1808/15869

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Studies of rotational predissociation of van der Waals molecule by the method of complex coordinate

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A practical method is presented for calculating resonance energies and widths (lifetimes) of metastable states of van der Waals molecules, incorporating the use of complex coordinate transformation and square-integrable basis functions. The utility of the method is illustrated through a study of the level widths and energies of rotationally predissociating atom–diatom model systems. Satisfactory agreement with previous works was found. Besides involving only bound state calculations and being free from imposement of boundary conditions, the method can be readily extendable to multichannel coupling problems.

I. INTRODUCTION

Recently the experimental investigation of structural features of van der Waals molecules, prepared by the supersonic free expansion method, has become increasingly important as a mean for accurately probing the nature of intermolecular forces. Detailed references in this field can be found in the review papers by Ewing[1] and a recent paper by Beswick *et al.*[2]

In the van der Waals molecules, the collisional or optical excitation process is well defined and can be well controlled, and the resulting dynamic intramolecular relaxation provides an interesting and unique example for vibrational or rotational predissociation in a single potential energy surface. In the present paper we are concerned with the prediction of resonance energies and widths (intrinsic lifetimes) of metastable states of van der Waals molecules. Such information is important to the elucidation of the general features of bond breaking processes in chemical systems where the predissociations occur 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 the molecular 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 Grabenstetter and Le Roy[4] and will not be elaborated here. The latter authors also proposed an "infinite wall" secular equation method which uses only L^2 (square-integrable) basis functions and the Fano theory for the mixing of a discrete state with a continuum.[4] In this paper we advance a method employing also only L^2 basis functions and the use of complex coordinate transformation.[5] 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 and is free from the uncertainties and sophistication associated with the estimation of level density in the secular equation method.[4] The complex coordinate

method,[5] 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 itself. It has been applied successfully to atomic resonances,[6] to dc Stark broadenings of atoms,[7] to ac Stark shifts and multiphoton ionizations of atoms,[8] to field ionization of atoms in crossed electric and magnetic fields,[9] to quasi-Landau resonances[9,10] and photoionization of atoms in a magnetic field,[10] and to molecular electronic resonances within the framework of the Born–Oppenheimer approximation.[11]

In the present work we focus on the application of the method of complex coordinate to the rotational predissociation of atom–diatom van der Waals molecules. The extension of the method to the aspect of vibrational predissociation will be treated in a subsequent paper. In Sec. II we present an outline of the proposed method. The utility of the method is then illustrated in Sec. III through quantitative comparisons with results obtained previously using other treatments. Finally, a brief summary of the merits of the current method is presented.

II. METHOD

A. Model Hamiltonian

The system under consideration consists of a diatomic rigid rotor BC with orientation $\hat{r}$ and a structureless atom A with position R relative to the center of mass of the diatom. The Hamiltonian for the atom–diatom complex, within the Born–Oppenheimer approximation, can be represented by[4,12]

$$H(R, \theta) = \frac{1}{2\mu}\left(-\hbar^2 \frac{\partial^2}{\partial R^2} + \frac{l^2(\hat{R})}{R^2}\right) + B_{\text{rot}} \cdot \mathbf{j}^2(\hat{r}) + V(R, \theta) . \tag{2.1}$$

In this equation $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$, $\cos\theta = \hat{r} \cdot \hat{R}$, $B_{\text{rot}} = $ rotational constant of the diatom, $\mathbf{j} = $ rotational angular momentum of BC, $\mathbf{l} = $ orbital angular momentum of BC and A about each other, and $V(R, \theta) = $ interaction potential of A and BC. The potential energy can be expanded in terms of the Legendre polynomials $P_k(\cos\theta)$,

$$V(R, \theta) = \sum_{k=0}^{\infty} V_k(R) P_k(\cos\theta) . \tag{2.2}$$

In the total angular momentum (J, M) representation,

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$J = l + j$, a convenient angular basis for wave function expansion is the total angular momentum eigenfunction defined by[13]

$$\mathcal{Y}^M_{Jlj}(\hat{R}, \hat{r}) = \sum_{m_l} \sum_{m_j} (ljm_lm_j|ljJM)$$
$$\times Y_{lm_l}(\hat{R}) Y_{jm_j}(\hat{r}) , \qquad (2.3)$$

where $(\cdots|\cdots)$ is the Clebsch–Gordan coefficient and Y_{km_k} is the spherical harmonics. It is expedient to define a scheme[12] for labeling of the eigenstates of the complex uniquely. In the isotropic limit, the potential energy is independent of θ and only $V_0(R)$ is retained in the Hamiltonian. Each isotropic state is then an eigenfunction of j^2, l^2, J^2, and J_z and may be labeled by $|jlJM\rangle$. The latter may be decomposed into a radial and an angular functions

$$|jlJM\rangle = \phi_{Jlj}(R) \mathcal{Y}^M_{Jlj}(\hat{r}, \hat{R}) . \qquad (2.4)$$

Owing to the spherical harmonic properties of the angular function, the isotropic state has a definite parity of $(-1)^{j+l}$ (If the diatom is a homonuclear molecule, there is an additional symmetry of inversion of $\hat{r}$). When the potential anisotropy is turned on, the state will be only an eigenfunction of J^2 and J_z and of the same inversion parity $(-1)^{j+l}$. Nevertheless the noncrossing rule ensures that the energy level for a fixed J and M value and $(j + l)$ parity will not cross. At any value of the anisotropic parameter the energy ordering of the states is the same as the ordering in the isotropic limit. Thus the isotropic function $|jlJM\rangle$ forms a convenient unperturbed basis for our present study.

The predissociation resonances associated with the atom–rigid-rotor diatom complex can be qualitatively understood as follows. During a low (subexcitation) energy molecular collisions, 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 "quasibound" van der Waals complex. The width of the complex is associated with the dissociation of the van der Waals molecule which occurs when the internal energy is reconverted into the relative translational energy along the atom–diatom van der Waals bond and the fragments separate. In the present case of atom–

rigid-rotor diatom, the predissociation width is induced by the potential anisotropy. In Sec. II B we present a method for determining the energies and widths of such metastable levels.

B. Method of complex coordinates and L^2 basis function expansion

According to the theory of dilatation transformation,[5–11] the energy (E_R) and the width (Γ) associated with a metastable state may be determined by the solution of the complex eigenvalue of a non-Hermitian Hamiltonian $H_\alpha(R, \theta)$, obtained by applying the dilatation or complex-coordinate transformation,[5] $R \rightarrow R\exp(i\alpha)$, to the real Hamiltonian $H(R, \theta)$. That is,

$$H(R, \theta) \xrightarrow{R \rightarrow Re^{i\alpha}} H_\alpha(R, \theta)$$
$$= e^{-2i\alpha} \frac{1}{2\mu} \left(-\hbar^2 \frac{\partial^2}{\partial R^2} + \frac{l^2}{R^2}\right) + B_{rot} j^2$$
$$+ \sum_k V_k(Re^{i\alpha}) P_k(\cos\theta) , \qquad (2.5)$$

where α is usually taken to be a positive number. In the present study, the total wave function of the Hamiltonian $H_\alpha(R, \theta)$, for a given J and M, will be expanded in terms of the complete set of the isotropic state functions $|jlJM\rangle$ allowed by the symmetry. We further expand the radial function $\phi_{Jlj}(R)$ of $|jlJM\rangle$ in terms of an orthonormalized L^2 (square-integrable) basis function $[\chi_n(R)]$,

$$\phi_{Jlj}(R) = \sum_{n=1}^{N_\gamma} a_n(\gamma) \chi_n(R) , \qquad (2.6)$$

where γ specifies the channel quantum number, $\gamma = (jlJM)$, N_γ is the size of the truncated radial basis, and $\langle \chi_n|\chi_m \rangle = \delta_{nm}$. For convenience, let us define the basis function

$$|\gamma n\rangle \equiv \chi_n(R) \mathcal{Y}^M_{Jlj}(\hat{r}, \hat{R}) \qquad (2.7)$$

and arrange the order of the matrix elements of $H_\alpha(R, \theta)$ in such a way that n is allowed to vary from 1 to N_γ within each channel $\gamma = (jlJM)$. The matrix element in the $|\alpha n\rangle$ representation is

$$\langle \gamma' n' | H_\alpha(R, \theta) | \gamma n \rangle = e^{-2i\alpha} \frac{\hbar^2}{2\mu} \langle \chi_{n'} | -\frac{d^2}{dR^2} + \frac{l(l+1)}{R^2} | \chi_n \rangle \delta_{ll'}\delta_{jj'}\delta_{JJ'}\delta_{MM'}$$

$$+ B_{rot} j(j+1)\hbar^2\delta_{ll'}\delta_{jj'}\delta_{nn'}\delta_{JJ'}\delta_{MM'} + \sum_k \langle \chi_{n'} | V_k(Re^{i\alpha}) | \chi_n \rangle f_k(l'j', lj; J)\delta_{JJ'}\delta_{MM'} . \qquad (2.8)$$

where f_k is the Percival–Seaton coefficient.[14] The resulting matrix of H_α is a symmetric complex matrix whose complex eigenvalues can be determined via the secular determinant

$$\text{Det} |(H_\alpha)_{\gamma'n',\gamma n} - EI| = 0 . \qquad (2.9)$$

The desired metastable states are then identified by the stationary points[6,7] of the α trajectories of complex eigenvalues.

III. CALCULATIONS AND DISCUSSIONS

To assess the usefulness of the outlined procedure in Sec. II, we discuss below the application of this technique to the determination of energies and widths of two A–BC model systems for which previous data are available for comparison. The systems under consideration have the following potential energy form

$$V(R, \theta) = V_0(R) + V_2(R) P_2(\cos\theta) , \qquad (3.1)$$

TABLE I. Parameters characterizing the van der Waals model systems studied in the present work.

	System A[a]	System B[b]
μ(amu)	1.340 15	1.340 15
B_{rot} (cm^{-1})	60.967	60.967
ϵ(cm^{-1})	384.097	384.097
σ(Å)	3.00	3.00
a	0.15	−0.4

[a]See also Ref. 4.
[b]See also Refs. 4 and 15.

with

$$V_0(R) = 4\epsilon\left[(\sigma/R)^{12} - (\sigma/R)^6\right], \qquad (3.2)$$

and

$$V_2(R) = 4\epsilon a(\sigma/R)^{12}, \qquad (3.3)$$

where a is the anisotropic parameter. The values of the parameter used are listed in Table I.

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. As in previous works[4,15] we limit the angular basis with $j \leqslant 2$, and $J = M = 0$. Thus only a single closed channel ($j = 2$, $l = 2$, $J = 0$, $M = 0$) and a single open channel ($j = 0$, $l = 0$, $J = 0$, $M = 0$) are allowed by the symmetry. The metastable state in this case correlates with the isotropic channel $|j = 2,\ l = 2,\ J = 0,\ M = 0\rangle$.

The matrix of interest in the $|\gamma n\rangle$ representation is thus of two by two block form (Fig. 1). Within each diagonal block specified by the channel quantum number $\gamma = (jlJM)$, we use the orthonormal harmonic oscillator L^2 basis

$$\chi_n(R) = \left(\frac{\beta}{\pi^{1/2} 2^n n!}\right)^{1/2} H_n(\beta x) \exp(-1/2\beta^2 x^2) \qquad (3.4)$$

to expand the radial wave function $\phi_{Jlj}(R)$ defined in Eq. (2.6). It is well known[17] that the harmonic oscillator basis provides a compact analytic representation for the complete set of bound and continuum states of an anharmonic oscillator in the inner radial region. In Eq. (3.4), H_n is a Hermite polynomial, $x = R - R_0$, and β is a disposable nonlinear parameter. To avoid the singulari-

$\langle j{=}l{=}2,\ n\,|\,H\,|\,j{=}l{=}2,n'\rangle$	$\langle j{=}l{=}2,n\,|\,V_2P_2\,|\,j{=}l{=}0,n'\rangle$
$\langle j{=}l{=}0,n\,|\,V_2P_2\,|\,j{=}l{=}2,n'\rangle$	$\langle j{=}l{=}0,\ n\,|\,H\,|\,j{=}l{=}0,n'\rangle$

$(n,n' = 1, 2, \ldots, N)$

FIG. 1. Matrix structure of the predissociation Hamiltonian H in the $|\gamma n\rangle$ representation. Here $\gamma = (jl,\ J{=}M{=}0)$ specifies the channel quantum number, n is the index number for the harmonic oscillator radial basis, $n = 1,\ 2,\ \ldots,\ N$, and V_2P_2 is the anisotropic potential.
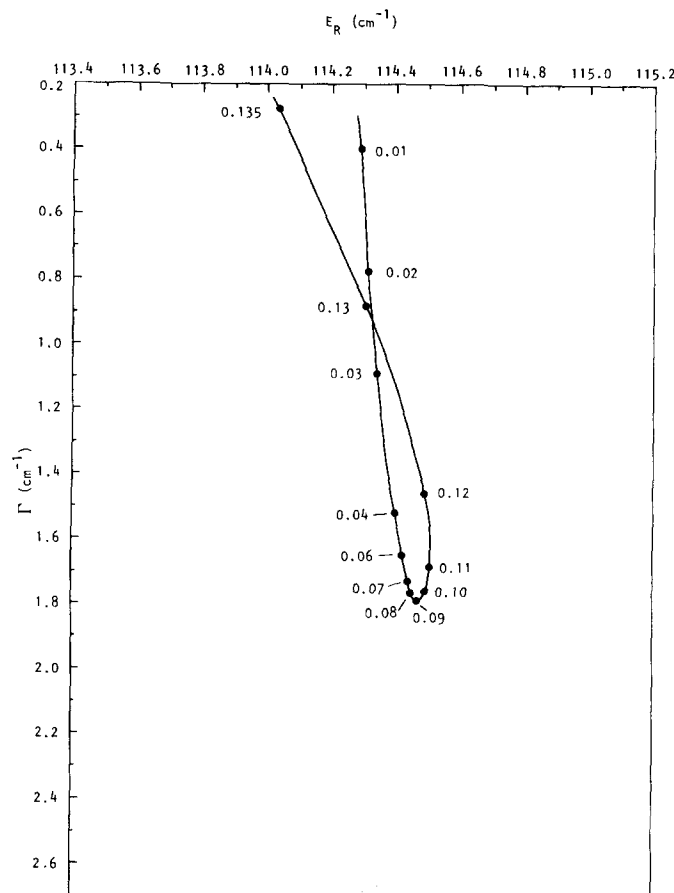

FIG. 2. α-trajectory for the complex eigenvalue associated with the rotational predissociation of the metastable level ($j = l = 2$, $J = M = 0$) of the atom–diatom van der Waals model system A. The numbers shown in the figure indicate the rotational angles α (in radians) used.

ty of the R^{-m} ($m = 2, 6, 12$) potential at $R = 0$, we adopt an accurate procedure devised by Harris et al.[18] to evaluate the matrix elements of $\langle \chi_{n'}|R^{-m}|\chi_n\rangle$. Thus

$$\langle \chi_{n'}|R^{-m}|\chi_n\rangle \simeq \sum_{s=0}^{N} T_{n's} T_{ns} \left(\frac{\xi(s)}{\beta} + R_0\right)^{-m}. \qquad (3.5)$$

Here $\mathbf{T} = (T_{pq})$ is the orthogonal matrix which diagonalizes the matrix (ξ_{pq}) of the operator $\xi = \beta x = \beta(R - R_0)$ in the harmonic oscillator basis of truncated size N, and $\xi(s)$ is the corresponding s^{th} eigenvalue. Dickinson and Certain[19] showed that such a procedure is equivalent to a Gaussian quadrature.

For both systems, we use $R_0 = 2^{1/6}\sigma$, and $\beta = 2.0\ a_0^{-1}$ ($a_0 = $ Bohr radius). To compare with secular equation method of Grabenstetter and Le Roy[4] who used 20 box-normalized radial basis functions, we also set $N = 20$ for both channel blocks of Fig. 1. The symmetric complex matrix of Fig. 1 was diagonalized and the complex eigenvalue correlated with the closed channel ($j = l = 2$, $J = M = 0$) was found. In Figs. 2 and 3, the α trajectories of the desired complex eigenvalue are plotted for system A and B, respectively. For system A (Fig. 2), the resonance location is clearly identified by the sharp turning point of the α trajectory nearby $\alpha \approx 0.09$ radian. We estimate the resonance energy and width to

be $E_R(\text{cm}^{-1}) \simeq 114.47$ and $\Gamma(\text{cm}^{-1}) \simeq 1.79$. For system B (Fig. 3), the turning point, though less sharp than system A, occurs nearby $\alpha \approx 0.124$ radian where $|\Delta\Gamma/\Delta\alpha|$ reaches the minimum and we obtain $E_R(\text{cm}^{-1}) \simeq 90.0$ and $\Gamma(\text{cm}^{-1}) \simeq 28.2$. The somewhat slower convergence for system B can be attributed to its larger anisotropy. This implies larger basis set is required for system B to achieve the same accuracy of system A. In Table II, the results of the present work are compared with previous theoretical data.[4,15,16] The overall agreement seems satisfactory, expecially with the close coupling results.[4,15] This justifies the reliability of the present method.

In the present study, the intermolecular potential was chosen[15] to be the simplest realistic form exhibiting atom–homonuclear diatomic molecule. The rotational constant B_{rot} was chosen to be that of H_2 and the reduced mass corresponds to He–H_2 collisions.[15] We point out, however, that the applicability of the present method is independent of the mass, rotational constant, anisotropy and energy parameters used and should be equally applicable to atom–heteronuclear diatomic molecule. Extension of the method to the rotational predissociation of atom–polyatom and diatom–diatom van der Waals molecules would be interesting and involves only different angular momentum coupling algebra.

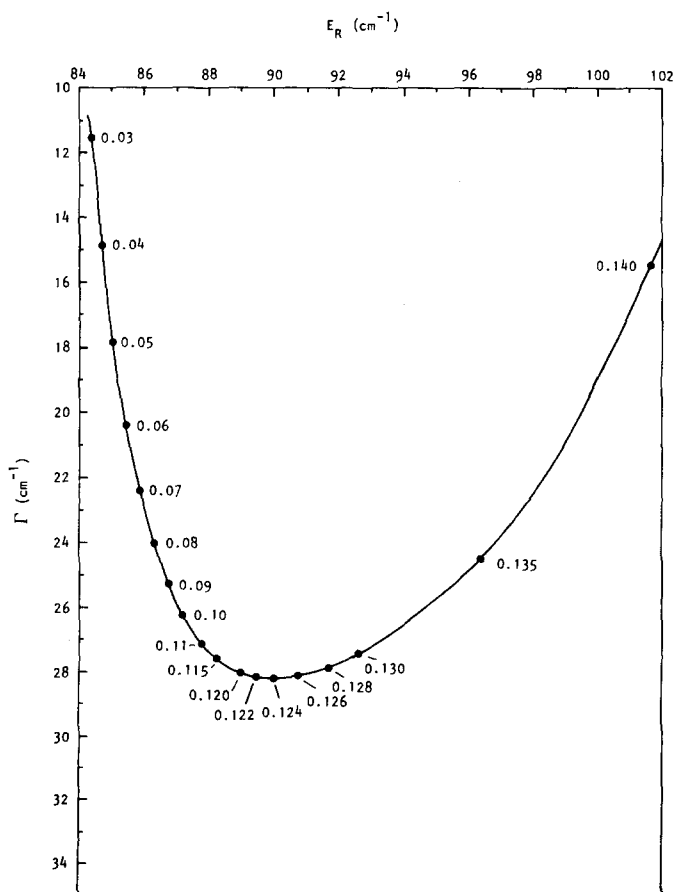In comparing with other theoretical treatments of the

TABLE II. Comparison of resonance energies and widths determined by various methods.

Method	System A		System B	
	$E_R(\text{cm}^{-1})$	$\Gamma(\text{cm}^{-1})$	$E_R(\text{cm}^{-1})$	$\Gamma(\text{cm}^{-1})$
CC[a]	114	2.09	88.2	27
SE[b]	114.46[±0.04]	2.40[±0.08]	86.5[±0.5]	28.0[±0.9]
A[c]	114[±1][f]	1.8[±0.7][f]	81.6[±0.5][f]	35[±2][f]
D[d]	114[f]	1.8[±0.7][f]	60.7[f]	45[±2][f]
CR[e]	114.47	1.79	90.0	28.2

[a]Numerical solution of coupled equation of Ref. 15.
[b]Secular equation method of Ref. 4.
[c]Adiabatic decoupling approximation of Refs. 15 and 16.
[d]Distortion decoupling approximation of Refs. 15 and 16.
[e]Complex coordinate rotation method; present work.
[f]Data quoted in Ref. 4.

same problem, several advantages of the current method may be realized.

(i) It is an *ab initio* method (given a defined Hamiltonian).

(ii) Only bound state and finite matrix calculations are involved.

(iii) No asymptotic boundary conditions need to be enforced.

(iv) Extension to multichannel problem (i.e., higher collisional energy regimes where more than one open and one closed channels are involved) is readily obtained by simply including more symmetry-allowed channel "blocks" in Fig. 1. This is a distinct advantage over, for example, the secular equation method[4] where sophisticated estimation of the level density is required.

In summary, we have shown in this paper that the method of complex coordinate, when coupled with the use of appropriate symmetry allowed L^2 basis expansion, provides a simple, efficient, and reliable method for studying the rotational predissociation of van der Waals complex. Extension of the present approach to the problem of vibrational predissociation is underway.

ACKNOWLEDGMENTS

FIG. 3. As in Fig. 2, for the strongly anisotropic model system B.

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