Rotational resonance states of Ar–HCl($\nu=0$) by finite range scattering wave function method

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The low lying rotational resonance states of Ar–HCl van der Waals molecule in the vibrational ground state of HCl are calculated for several total angular momentum states within the model of a rigid rotor-atom system. The necessary scattering calculations are done by the finite range scattering wave function (FRSW) method [J. Chem. Phys. 99, 1057 (1993)] adopting energy independent auxiliary functions which makes the scattering calculations at many energies much more efficient. Discrete eigenvectors and eigenvalues of Hamiltonian matrix are calculated on a finite range via the successive diagonalization-truncation scheme combined with the discrete variable representation (DVR). Analytical eigenfunctions of the asymptotic Hamiltonian operator in a body-fixed frame excluding only the interaction potential, but including all the effective centrifugal potential terms, are used as asymptotic wave functions, which reduces the dynamical range required for the $\mathcal{L}^2$ scattering calculations. After a single diagonalization of the Hamiltonian in the finite range $\mathcal{L}^2$ representation, resonance parameters are extracted through the energy dependence of Smith's lifetime matrix. A search algorithm for multiple resonances is used assuming constant background effects and isolated, simple resonances. Several recommendations for the choice of the translational basis functions and the basis set ranges which target specific kinds of resonances with various accuracies are given. Resonance energies and widths (lifetimes and partial decay probabilities) for many predissociating states of Ar–HCl are given with unprecedented accuracy.

I. INTRODUCTION

The exact time independent quantum mechanical methods to study molecular resonance states include the stabilization method, the complex rotation/scaling methods, and the optical potential method which are full $\mathcal{L}^2$ basis set methods. In these methods, many resonance positions and total widths are determined simultaneously. This feature may be convenient when many resonance states are concerned. However, in all of these approaches, real or complex Hamiltonian matrices, expanded in basis sets for all degrees of freedom including the dissociative coordinate, have to be diagonalized many times in order to obtain accurate positions and widths of resonances. In particular, they require changing calculational parameters, such as basis function parameters, complex rotation angles, or the optical potential, before the accurate values of the resonance parameters are obtained.

On the other hand, we may use methods which focus on resonances on a given narrow energy range such as the methods of eigenphase, S matrix parameterization, and lifetime matrix. They produce parameters for each resonance state one by one through a series of S matrix ($S$) and/or energy differentiated S matrix ($dS/dE$) calculations around each resonance energy. All require scattering calculations which can be done in a variety of ways. In the propagation methods, such as close-coupled equations with R matrix or log-derivative matrix propagation, the Hamiltonian matrix is expanded locally in the internal states which are coupled and the solutions are then propagated from deep inside the interaction potential region to the asymptotic region where the scattering information is extracted. In these methods, the direct product basis set is one dimension smaller than that of the full $\mathcal{L}^2$ basis set methods, since the dissociative coordinate is not represented by a basis set. The propagation of the solution has to be repeated for each energy. This feature may be advantageous when the resonance states can be determined by relatively few energy scattering calculations. This is especially true when the approximate location of the resonance is already known and/or, only a few resonance states are desired.

Other full $\mathcal{L}^2$ basis set scattering methods include the S matrix/log-derivative matrix Kohn variational ap...
proaches\textsuperscript{10,11} and the finite range scattering wave function (FRSW) method.\textsuperscript{12} In these methods, once the necessary energy independent integrals are evaluated, stored, and/or, perhaps better, the Hamiltonian matrix is diagonalized, the scattering calculation for each energy only involves several matrix multiplications, inversions, and/or a small number of energy dependent integral evaluations. Since the calculational cost per energy is relatively cheap, they may be suitable for multiple resonance state determinations which necessarily require scattering calculations at many energies.

A convenient feature of the lifetime matrix \( Q = -i \hbar \frac{dS}{dE} S^\dagger \) (Ref. 13) in studying resonances is that its parametric dependence on energy is simpler than that of the S matrix. In particular, the diagonal elements of \( Q \) are real because of Hermiticity and the background effects can be accurately treated assuming slow variation with energy. We also note that all partial widths can be determined from the diagonal elements of \( Q \) only. But, the price to pay for this convenience is the additional calculation of \( \frac{dS}{dE} \) as a function of desired scattering energy. One direct approach would be to do finite differencing (i.e., \( \Delta S/\Delta E \)) evaluated on a very fine energy grid. However, for most of the scattering calculational methods, it is rather straightforward to derive expressions for \( \frac{dS}{dE} \), and this is also the case for the FRSW method\textsuperscript{12} as well as some other \( L^2 \) and propagation methods.\textsuperscript{14,15} Consequently, the direct evaluation of \( \frac{dS}{dE} \) and thus the lifetime matrix \( Q \) may be adopted.

In this paper, the "energy independent integral" FRSW method,\textsuperscript{12} which results from using an energy independent auxiliary function, is used to calculate \( S, \frac{dS}{dE} \), and, subsequently, the lifetime matrix \( Q \) at many scattering energies. This then determines explicitly the resonance parameters [resonance energy \( (E_R) \), total width \( (\Gamma) \), and partial widths \( (\Gamma_i) \)] from the energy dependence of the lifetime matrix, \( Q \). In particular, the rotational resonances of the \( \text{Ar}-\text{HCl}(v=0) \) van der Waals molecule are investigated using the model of a rigid rotor-atom system. This model system has been investigated by Ashton, Child, and Hutson\textsuperscript{16} using R-matrix propagation and the eigenphase method to extract the resonance parameters from the time independent scattering calculations at many energies. More recently Choi and Light\textsuperscript{17} identified the resonances and determined very approximate lifetimes from a single \( L^2 \) diagonalization by applying the "flux operator" method. In this paper, we present the results of the FRSW method with energy independent auxiliary functions of Ref. 12. From now on we refer to this simply as the FRSW method.

The desirable features of the FRSW method for resonances are; first, once the real Hamiltonian matrix is diagonalized in a finite range \( L^2 \) basis and the required energy independent real integrals are evaluated, \( S \) and \( \frac{dS}{dE} \) are easily obtained at each energy. They are obtained by operations on integrals and small matrices (order of twice the number of open channels, not of the number of basis functions) such as summations, multiplications and inversions. Second, no additional integrals are needed in order to calculate \( dS/dE \) besides the ones already used to calculate \( S \). Third, the bound states of the system are obtained as byproducts because of the real Hamiltonian matrix diagonalization. Fourth, the translational basis set range may be restricted to be smaller than that required to reach the fully asymptotic region, thus reducing the translational basis set size. In this case the value of trace \( Q \) is obtained accurately by averaging over one wavelength of oscillation of the trace \( Q \) as a function of the position of "asymptotic" evaluations. Finally, regular boundary conditions for the scattering wave functions are easily imposed by placing the origin of the linear translational auxiliary function at the inner boundary of the basis set range.

In the remainder of the paper, the detailed description of the FRSW method applied to the model of rigid rotor-atom inelastic scattering/resonance in a body-fixed frame is given in Sec. II. This is followed by a brief explanation of the multiple resonance state search algorithm and computational details in Sec. III. The numerical results for various resonance features are examined with respect to the various calculational parameters, and comparisons with results of the flux-operator method by Choi and Light and those of the eigenphase analysis by Ashton et al. are given in Sec. IV. Several recommendations about the choice of the calculational parameters are given along with the conclusions of this paper in Sec. V. In the Appendix, the erratic oscillation of trace \( Q \) near the basis set boundary is discussed.

II. FRSW METHOD FOR RIGID ROTOR-ATOM SYSTEM

In this section, the detailed equations of the FRSW method applied to the resonances of the rigid rotor-atom system are derived. The general procedures are that we (1) set up the Hamiltonian operator in a body-fixed frame; (2) choose the real \( L^2 \) basis sets and diagonalize the Hamiltonian matrix; (3) evaluate the necessary energy independent integrals composed of the discrete eigenvectors, Hamiltonian operator, energy independent auxiliary functions, and asymptotic eigenfunctions; (4) solve the system of linear equations for \( S \), the coefficient matrix \( C, \frac{dS}{dE} \), and \( dC/dE \) at each energy, which is obtained from imposing the asymptotic boundary conditions; (5) construct \( Q \) from \( S \) and \( \frac{dS}{dE} \) and determine the resonance parameters \( (E_R, \Gamma, \Gamma_i) \) from the energy dependence of the \( Q \) matrix.

Since the details of the Hamiltonian operator in the body-fixed frame and the basis function expansions of wave functions are described in detail elsewhere,\textsuperscript{17-19} only the essential results are repeated here with minor modifications of notations. The body-fixed frame \( xyz \) is defined by three Euler angles \( \chi, \psi, \omega \) of which \( \chi, \psi \) are determined by the orientation of the body-fixed \( z \) axis in space, and \( \omega \) is set such that the plane of the system coincides to the \( xz \) plane of the body-fixed frame. The body-fixed \( z \) axis connects the center of mass of the rigid rotor and the atom. See Ref. 18 for more details of this coordinate frame. The Hamiltonian operator for a rigid rotor-atom system using mass scaled Jacobi coordinates is given by
\[
\hat{H}(R, \theta, \chi, \psi, \omega) = \frac{-1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{4\mu R^2} \left[ \frac{-1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \hat{J}_z^2 + \hat{J}_z^2 - 2 \hat{J}_z \right] + \frac{1}{2\mu R^2} \left[ \cot \theta (\hat{J}_z + \hat{J}_z^-) \hat{J}_z - \frac{\partial}{\partial \theta} (\hat{J}_z + \hat{J}_z^-) \right] + D_{\text{rot}} \left( \frac{-1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \hat{J}_z^2 \right) + V(R, \theta),
\]

where

\[
P_{\text{rot}} = \frac{1}{2\mu r_e^2},
\]

with the volume element \( d\tau = dR \sin \theta \, d\theta \, d\chi \sin \psi \, d\psi \, do \) and \( \tilde{n} = 1 \). The \( \mu \) is the reduced mass of the system, \( R \) is the mass scaled Jacobi coordinate representing the dissociative coordinate, \( \theta \) is the angle between the body-fixed \( z \) axis and the rigid rotor axis, \( r_e \) is the length of the rigid rotor, and \( V(R, \theta) \) is the interaction potential. The angular momentum operators are defined consistently in the body-fixed frame, but they follow the normal commutation relations, consequently the raising and lowering operators act on the Wigner rotation functions as in Eq. (2)

\[
\hat{J}_z^+ D_{K\chi}(\chi\psi\omega) = -\Lambda_{JK}^+ D_{K+1\chi}(\chi\psi\omega),
\]

\[
\hat{J}_z^- D_{K\chi}(\chi\psi\omega) = -\Lambda_{JK}^- D_{K-1\chi}(\chi\psi\omega),
\]

The asymptotic Hamiltonian operator \( \hat{H}_0 - \hat{V}(R, \theta) \) has analytic eigenfunctions defined as

\[
\Psi_{JM}(\chi\psi\omega) = \sqrt{\frac{2^{2J+1}}{4\pi}} \sum \mathcal{C}(JU) \Lambda_0 \Lambda
\]

\[
\times Y_{J\lambda}(\chi\psi\omega) Y_{J\lambda}(\theta, \psi),
\]

where \( \hat{J}_z^{[1,2]}(k, R) \) are the Riccati–Hankel functions of outgoing and incoming waves, \( C(\cdots | \cdots) \) is the Clebsch–Gordan coefficient, and the \( Y_{J\lambda}(\theta, \psi) \) are spherical harmonics. By applying the asymptotic Hamiltonian operator \( \hat{H}_0 - \hat{V}(R, \theta) \) where \( \hat{H} \) is as in Eq. (1) to the function of Eq. (3), and rearranging the terms using properties of Clebsch–Gordan coefficients, it can be confirmed that Eq. (3) is indeed an eigenfunction of the asymptotic Hamiltonian operator written in the body-fixed frame. The total angular momentum \( J \), its space-fixed \( Z \) component \( M \), and parity \( p \) \((=0,1)\) are strictly conserved; moreover, the rigid rotor angular momentum \( j \), and the orbital angular momentum \( l \) are conserved asymptotically, so they can be used to denote a specific scattering wave function. Henceforth, quantum numbers \( J, M, \) and \( p \) will be suppressed to simplify notation where appropriate. The normalized discrete eigenfunctions of the total Hamiltonian operator with angular momenta \( J, M, \) and parity \( p \) are expanded by direct product DVR basis functions (except for the overall rotation) as

\[|m(R, \theta, \chi, \psi, \omega)\rangle = \sum a_{\alpha K}^m \cdot |R_{\alpha}(R)\rangle \cdot |\theta_{\beta}^{(2)}(\theta)\rangle \cdot \mathcal{C}_{KM}^p(\chi\psi\omega),\]

where \( a_{\alpha K}^m \) is the expansion coefficient, \( |R_{\alpha}(R)\rangle, |\theta_{\beta}^{(2)}(\theta)\rangle \) are the DVR basis functions based on translational basis functions with zero boundary conditions (to be specified later) and normalized associated Legendre polynomials, respectively. Note that we will use the same notation for DVR basis function and its corresponding DVR point (Gaussian quadrature point). The overall rotations are expanded in parity adapted normalized rotation functions \( \mathcal{C}_{KM}^p(\chi\psi\omega) \) which are eigenfunctions of \( \hat{J}_z, \hat{J}^2 \), and the parity operator \( \hat{p} \) with the eigenvalues of \( J^2, M, \) and \((-1)^p\) respectively. They are defined by

\[
\mathcal{C}_{KM}^p(\chi\psi\omega) = \mathcal{N}_{JK} \left[ (-1)^p \hat{D}_{KM}^J(\chi\psi\omega) \right]
\]

\[
\mathcal{N}_{JK} = \frac{1}{4\pi} \sqrt{\frac{2^{2J+1}}{1 + (-1)^{(J+p)}}} \Delta_{J\lambda}^K.
\]

where \( K \) is non-negative integer ranging from 0 or 1 to \( J \) \[zero is not allowed for odd \((J+p)\) state\]. The Hamiltonian matrix elements are given, in this representation, by

\[
H_{\alpha\beta, K' \alpha K} = \langle R_{\alpha'} \cdot \theta_{\beta'}^{K'} \cdot \mathcal{C}_{K'M}^{p'} | \hat{H} | R_{\alpha} \cdot \theta_{\beta}^K \cdot \mathcal{C}_{KM}^p \rangle
\]

\[
= -\frac{1}{2\mu} \frac{d^2}{dR^2} \delta_{\beta'} \delta_{\alpha'} \delta_{K'} + \frac{1}{2\mu R^2} \left[ \mathcal{N}_{JK} \cdot \Lambda_{JK}^+ \cdot \mathcal{C}_{K'+1}^p \delta_{\beta' \alpha'} \cdot \delta_{K' \lambda} + \mathcal{N}_{JK} \cdot \Lambda_{JK}^- \cdot \mathcal{C}_{K'-1}^p \delta_{\beta' \alpha'} \cdot \delta_{K' \lambda} \right] + B_{\alpha \beta} \delta_{\alpha' \alpha} \delta_{K' \lambda} \delta_{\beta' \beta} \delta_{K' \lambda} + V(R_{\alpha} \delta_{\beta}^K) \delta_{\alpha' \alpha} \delta_{\beta' \beta} \delta_{K' \lambda}.
\]
where

\[ \mathbf{d}_{\alpha} = \sum_{i,j} \mathbf{T}_{\alpha} \cdot \left( \frac{d^{2}}{dR^{2}} \varphi(R) \right) \cdot \mathbf{T}_{\alpha} \]

\[ \mathbf{b}_{\beta} = \sum_{j} \mathbf{T}_{\beta} \cdot j(j+1) \cdot \mathbf{T}_{\beta} \]

\[ \mathbf{b}_{\gamma} = \sum_{j} \mathbf{T}_{\gamma} \cdot \mathbf{T}_{\gamma} \cdot \mathbf{T}_{\gamma} \]

\[ \mathbf{S}_{\alpha} = \mathbf{S}_{\alpha} \mathbf{S}_{\alpha} \]

\[ \mathbf{N}_{K} = \sqrt{1+\delta_{K}} \]

The \( \mathbf{T} \) is the FBR-DVR transformation matrix between the translational basis functions \( \{ \varphi(R) \} \) and DVR basis functions \( \{ \mathbf{Y}_{i}(R) \} \), and \( \mathbf{b} \) is for the normalized associated Legendre polynomials \( \{ P_{j}^{(j)}(\cos \theta) \} \) and the angular DVR basis functions \( \{ \mathbf{Y}_{j}(\theta) \} \).

This representation of the Hamiltonian is diagonalized according to the successive diagonalization-truncation (SDT) scheme to get the discrete eigenvectors and eigenvalues. Because of parity conservation, even parity states \( \psi_{\alpha} \) dissociate exclusively into even \( \psi_{\alpha} \) states, and odd parity states \( \psi_{\alpha} \) into odd \( \psi_{\alpha} \) states. The next step is to derive expressions for \( \mathbf{S} \) and \( \frac{d\mathbf{S}}{dE} \).

The accurate scattering wave functions with \( N_{\text{open}} \) open channels defined on a finite range of the dissociative coordinate can be expanded by \( N_{\text{open}} \) linearly independent real finite range scattering wave functions \( \mathbf{Y}_{\alpha} \) which are conveniently named the "unnormalized FRSW." Thus we have

\[ \Psi_{\alpha} = \sum_{j,l} \Phi_{j,l} \cdot C_{j,l} \cdot \mathbf{Y}_{\alpha} \]

where the wave function is denoted by incoming rotational state \( (j,l) \). Each linearly independent \( \Phi_{j,l} \) can be constructed by choosing the auxiliary function as a product of translational auxiliary function \( f(R) \) and \( j, l \) asymptotic rotational state \( \varphi_{j,l}(\psi_{X}, \psi_{\theta}) \) such as

\[ \Phi_{j,l} = \sum_{m} [m] \cdot [m] \cdot [m] \cdot f(R) \cdot \varphi_{j,l}(\psi_{X}, \psi_{\theta}) \]

where \( f(R) \) increases linearly from zero at the inner boundary \( (R) \) of the translational basis functions toward outer boundary \( (R) \). Thus \( f(R) \) permits the scattering wave functions \( \Psi_{\alpha} \) to satisfy regular boundary conditions at the inner boundary. The expansion coefficients \( C_{j,l} \) and S-matrix elements \( S_{j,l} \) are determined by the asymptotic behavior of the scattering wave function:

\[ \Psi_{j,l} \sim \sum_{m} [m] \cdot [m] \cdot f(R) \cdot \varphi_{j,l}(\psi_{X}, \psi_{\theta}) \]

(8)

where \( f(R) \) increases linearly from zero at the inner boundary \( (R) \) of the translational basis functions toward outer boundary \( (R) \). Thus \( f(R) \) permits the scattering wave functions \( \Psi_{j,l} \) to satisfy regular boundary conditions at the inner boundary. The expansion coefficients \( C_{j,l} \) and S-matrix elements \( S_{j,l} \) are determined by the asymptotic behavior of the scattering wave function:

\[ \Psi_{j,l} \sim \sum_{i,j} \mathbf{T}_{i} \cdot \mathbf{T}_{j} \cdot \mathbf{T}_{i} \cdot \mathbf{T}_{j} \cdot \mathbf{T}_{i} \cdot \mathbf{T}_{j} \]

(9)

Note that no new matrices are needed in Eq. (12) besides the ones already calculated for the S-matrix calculation in Eq. (11). The actual calculation of \( \mathbf{S} \) and \( \frac{d\mathbf{S}}{dE} \) is done by, first, combining Eq. (10) evaluated at two adjacent DVR points, say \( R_{1} \) and \( R_{2} \), and solving for \( \mathbf{S} \) and \( \frac{d\mathbf{S}}{dE} \):
The calculated $S$ satisfies $S \cdot S^* = S^* \cdot S$. Thus the lifetime matrix $Q$ evaluated at $(R_1, R_2)$ is simply obtained by

$$\begin{align*}
Q &= -i \frac{dS}{dE} \cdot S* = -i \frac{dS}{dE} \cdot S^{-1} = -i \frac{dS}{dE} \cdot S^*.
\end{align*}$$

(15)

Since $S$ calculated from Eq. (13) is not required to be unitary, the $Q$ in Eq. (15) is not strictly Hermitian. However, the imaginary part of the trace $Q$ is negligible compared to the real part. In the following we use only the real part of $Tr Q$ to simplify the calculational procedures.

This concludes the derivations of the main working equations for the lifetime matrix calculation as a function of scattering energy and evaluation points of Eqs. (13) and (14) (loosely speaking, equivalent to our asymptotic positions).

### III. MULTIPLE RESONANCE STATES SEARCH ALGORITHM

Using the calculation of $Q(E)$ detailed in Sec. II, a practical algorithm is presented to determine resonance parameters not only for one resonance state but for almost all which may exist in the energy range of concern. This analysis below assumes that the resonances are simple, isolated resonance is,25

$$S(E) = S_0(E) - i \frac{t \cdot t^T}{E - \left( E_R - i \frac{\Gamma}{2} \right)}, \quad t_i = \sqrt{\Gamma} e^{i \phi_i},$$

(16)

where $S_0(E)$ is the nonresonance background contribution which is a slowly varying function of energy. Since $Q(E)$ is Hermitian, the diagonal elements are real which are the only quantities necessary for calculation of resonance parameters. If $Q_0(E)$ can be assumed to be constant across a resonance, one simple way of determining the resonance parameters is to find the energy where $Tr Q$ is locally maximum, such that,

$$Tr Q(E_{max}) = Tr Q_0 + \frac{4\hbar}{\Gamma}, \quad Q_{ii}(E_{max}) = Q_{0,ii} + \frac{4\hbar \Gamma_i}{\Gamma^2},$$

(18)

then $E_{max}$ is identified as the resonance position $E_R$, and $\Gamma$, $\Gamma_i$ are determined once $Q_0$ is evaluated.

Now, the remaining problems are, first, to find the accurate $Q$ as a function of energy, and, second, to estimate the rough locations of the resonance states on the real energy range of concern, otherwise an infinite number of energies have to be scanned to locate the resonances.

If the translational basis set range is large enough to encompass the asymptotic region, then the most accurate $Q$ is calculated if Eqs. (13) and (14) are solved at the outermost two DVR points (except for the case of Sturmian functions as translational basis). However a large range inevitably means a large size of basis set, and consequently, expensive computation.

It is observed phenomenologically that $Tr Q$ as a function of the positions at which Eqs. (13) and (14) are evaluated shows damping oscillation toward the outer end except for the energies just above a threshold. This oscillation is invariant of the basis set range and basis set size, and is a direct consequence of improving the asymptotic behavior on the wave functions where the interaction potential is not really zero. Also, it is related to the step-like phase shift of S-matrix elements as a function of asymptotic position and Levinson's theorem about the bound states (Ref. 12). The apparent wavelength of oscillation is half of that of the lowest translational energy channel wave function.

This observation suggests that the accurate estimation of $Q$ on a restricted basis set range may be obtained by averaging $Q$ over one wavelength of $Tr Q$ oscillation. Clearly this estimation is identical to the nonaveraged $Q$ in the case when the basis set range extends really to the asymptotic region and $Q$ is evaluated at the outermost DVR points. In practice, the wavelength is approximated by calculating the constant asymptotic wave number of the lowest translational energy channel, rather than tracing the actual coordinate dependent wavelength of the wave function. As a result, the averaged $Q$ itself shows also a damping oscillation with much smaller amplitude, so the best estimation may be the average of the outermost maximum and minimum averaged $Q$ with the error estimation being the difference of the two averages.
Also, the eigenvectors produced by the SDT scheme introduces some additional uncertainty in the Q matrix, which makes Tr Q deviate from the ideal damping oscillation as a function of asymptotic position. Quite interestingly, in this case the error is larger as the evaluation points approach the outer boundary. One possible explanation is given in the Appendix. In our actual calculations, a small region near the outer boundary is ignored in the averaging process for Tr Q. This prescription is demonstrated in Fig. 1. This averaging procedure is efficient especially for small Q (few open channels), which means low energy scattering. From now on, we use Q to refer to this double-averaged Q unless stated otherwise.

Since resonance states are pseudo bound states, they are well represented by basis state-like basis functions, and the resonance positions may be close to some of the discrete eigenvalues above dissociation energy. This is a basic idea of the stabilization method for resonances.1 Of course, in our $L^2$ basis most of such unbound state discrete eigenvalues correspond to just scattering states satisfying zero boundary condition at that specific basis set range. A typical Tr Q profile near a resonance is given in Fig. 2 with an arrow showing the corresponding discrete eigenvalue. This consideration leads to a search algorithm for determination of multiple resonance states starting from the unbound state discrete eigenvalues of the $L^2$ Hamiltonian matrix.

The major steps are (1) calculate Q at $E-E_m \pm \epsilon$ where $E_m$ is one of the unbound state discrete eigenvalues of H and, here, a small $\pm \epsilon$ is added to avoid an overflow error in the Green’s function of Eq. (11); (2) calculate the zeroth order total width $\Gamma$ assuming $Q_0$ is approximately zero; (3) search for a peak of Tr Q in the energy range of $[E_m - \Gamma, E_m + \Gamma]$; (4) if any peak is found, identify the peak energy as the resonance position $E_R$; (5) assume $Q_0$ is constant and calculate it by fitting Tr Q to the form of Eq. (17) around $E_R$, and determine $\Gamma$, and $\Gamma'$s by Eq. (18).

Three different kinds of translational basis functions are used; Sturmian, sine (i.e., Chebyshev polynomial of the second kind), and “inner” Lobatto shape functions (see Ref. 11). They are distinguished from each other primarily by the distribution pattern of quadrature points (DVR points), which may be characterized as, “denser toward the inner boundary,” “evenly spaced,” and “denser toward both boundaries,” respectively. The local distribution of quadrature points must be dense enough to support the maximum translational energy around that region to represent the wave function accurately. This requirement can be used to restrict the dissociative coordinate region for averaging the original Q, especially for Sturmian functions as basis. In the next section, the actual resonance parameters determined by the above algorithm are presented.

IV. NUMERICAL RESULTS

In this section, the parameters of the low lying rotational resonance states of the Ar–HCl($v=0$) van der Waals molecule are presented for several total angular momentum states. The scattering energy of concern ranges from 0.00 cm$^{-1}$ to 125.28 cm$^{-1}$ for even (J+p) states or from 20.88 cm$^{-1}$ to 125.28 cm$^{-1}$ for odd states (see Sec. II for quantum number definitions). The threshold for dissociation of the odd (J+p) states is 20.88 cm$^{-1}$ since they cannot decay to HCl(j=0). The energies are measured from the dissociation threshold of even states. The maximum number of open channels is six if resolved into (J,l) states, or three if resolved into (J) states (i.e., $j=0,1,2$). For this low energy range, the rigid rotor-atom model is valid for this system because the next excited state potential energy surface which correlates to HCl($v=1$) lies $\sim 3000$ cm$^{-1}$ above, so it does not affect the low energy dynamics.

The system parameters and the potential energy surface used in the actual calculations are given in Table I. The other calculational parameters of basis set, translational basis set range, range used for averaging the original Q and various cut parameters of the SDT scheme are presented in Table II. For most of the calculations, S is very nearly unitary. The calculated S has a unitarity error (defined in Ref. 12), $\Delta_U$, of $\sim 0.05$ in the worst case.
TABLE I. System parameters and potential energy surface.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mass</td>
<td>9.109 53 × 10^{-24} g</td>
</tr>
<tr>
<td>Hydrogen mass (H')</td>
<td>1.007 83 g/mol</td>
</tr>
<tr>
<td>Chlorine mass (Cl')</td>
<td>34.968 9 g/mol</td>
</tr>
<tr>
<td>Argon mass (Ar')</td>
<td>39.963 0 g/mol</td>
</tr>
<tr>
<td>Avogadro number</td>
<td>6.022 136 7 × 10^{23}/mol</td>
</tr>
<tr>
<td>Hartree energy</td>
<td>219 474 635 4 cm^{-1}</td>
</tr>
<tr>
<td>Bohr radius</td>
<td>0.529 177 06 Å</td>
</tr>
<tr>
<td>Equilibrium bond length of HCl(v=0)</td>
<td>1.283 87 Å</td>
</tr>
<tr>
<td>Potential energy surface</td>
<td>Hutson model H6(3)</td>
</tr>
</tbody>
</table>

Reference 26.

A restricted convergence test is done for the J=0 state by varying the outer boundary (R_f) and using three different basis sets of Table II. The results are given in Fig. 3 for several selected resonances. To get a broad picture about how the resonances are distributed along the full real energy range, Tr Q(E) as a function of energy is presented in Fig. 4 for J=0 state with a magnified vertical scale. The first feature to note is that there exist about twenty resonances with the lifetimes varying greatly. This is more pronounced for higher J states. The second thing is that the threshold effect largely caused by many bound states (16 states from Ref. 17) is not negligible. Thus the constant Q(0) approximation is not justified especially for very broad resonances (< ~ 1 ps) and/or the ones just above the thresholds; however, this energy region is also not suitable for Q averaging process, so accurate parameters may not be obtained for these kinds of resonances. The third thing is that several resonance states are overlapping especially just below a new threshold. This feature is more prominent for higher J states. Several consequences of overlapping resonances include multiple long-lived metastable states and nonexponential decay law.

A summary of our results is presented in Tables III and IV. The tables contain the positions and lifetimes of resonance states and their decay probabilities. The significant figures of the results are determined from the uncertainty in Tr Q evaluation. The resonance states with lifetimes γ > 0.1 ns for J=0, 1, and 10 are given in Table III. Also given in the table is a list of the positions and lifetimes of resonance states obtained using the flux-operator method as reported by Choi and Light (Ref. 17). The flux method is accurate in identifying the resonance positions; however, the estimated lifetimes are only informative in a qualitative sense.

Ashton et al. (Ref. 16) reported the resonance posi-

FIG. 3. Complex resonance energies (E_res = E_R - i γ/2) for R = 13, 14, 15, 16, 17 Å and three basis sets of Table II for J=0. Note that not all calculations detect a particular resonance. CPU times ratio is roughly 1:4:2 for basis S: basis T: basis L calculations as in Table II.

TABLE II. Calculational parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D_Pcut/N</td>
<td>Sturmian function DVR 45/60 (basis S)</td>
</tr>
<tr>
<td></td>
<td>Chebyshev polynomial of the second kind DVR 70/100 (basis T)</td>
</tr>
<tr>
<td></td>
<td>Lobatto shape function 65/80 (basis L)</td>
</tr>
<tr>
<td>NE</td>
<td>10</td>
</tr>
<tr>
<td>K_max</td>
<td>4 or J if J&lt;4</td>
</tr>
<tr>
<td>2D_Pcut(cm^{-1})</td>
<td>150.0</td>
</tr>
<tr>
<td>R_1 (Å)</td>
<td>3.0</td>
</tr>
<tr>
<td>R_2 (Å)</td>
<td>13.0, 14.0, 15.0, 16.0, 17.0</td>
</tr>
<tr>
<td>region for averaging Q (Å)</td>
<td>[5.0, min(R_f-1, R_{tot})]</td>
</tr>
</tbody>
</table>

* Nomenclature from Ref. 17.
* Maximum translational coordinate up to where the quadrature spacing could support the translational energy assuming its asymptotic value.

tions and widths of ArHCl ($J=0,1$) rotational resonances using the R-matrix close coupling calculation combined with eigenphase analysis and least-squares fit to the Breit-Wigner formula. Their resonance positions and total widths are compared with present ones for $J=0$ in Fig. 5. We note that two very long-lived translationally diffusive resonances found by Ashton et al. just below $J=1$ and $J=3$ thresholds do not appear in our calculation. The possible reasons for this are minor changes in the potential energy surfaces or, perhaps, that the resonance states extend beyond our $L^2$ basis set range. Although we cannot make precise quantitative comparison since the potential energy surfaces differ, we note the overall good qualitative agreement with the earlier results.

The partial widths agree less in a way that the earlier results show mostly "cold" HCl (which means that low $J$ is the major decay channel) for low energies, while the present results show rather randomized or "hot" HCl. This qualitative difference indicates that the partial widths are less sensitive to the details of potential energy surface than the positions or total widths.

The short-lived ($\tau<0.1$ ns) resonance states of $J=10$ are listed in Table IV. The production CPU times of present results on Stardent GS2000 computer are given in Table V with SDT scheme and resonance search results.

Referring to Table III, it seems that long-lived resonance states demand more of the basis set. Since their widths are extremely small (e.g., $0.6-0.8 \times 10^{-5}$ cm$^{-1}$ for 5.175 51 cm$^{-1}$ resonance of $J=10, p=0$), accurately converged results are more necessary than for the broader width cases (e.g., 0.003 56 cm$^{-1}$ for 18.0951 cm$^{-1}$ resonance of $J=10, p=0$). The accuracy of the lifetimes (or the resonance widths) of the extremely long-lived states are basically limited by the computational accuracy of the energy levels of the truly bound states. If the long-lived state, however, is more highly excited either in bending or stretching motions than all the bound states, the uncertainty in its lifetime may be due to not enough basis functions for the excited coordinate.

Due to the large anisotropy of the Ar–HCl interaction potential, $K$ is quite well-defined and the Coriolis coupling is relatively weak. In such cases, the zeroth order bound states are the bound eigenstates of the diagonal $K$ blocks. These bound states become resonance states when Coriolis coupling to the zeroth order unbound (or scattering) states of the neighboring $K'$ is included. Most of the narrow resonance states presented in Table III may originate from the bound zeroth order states of diagonal $K$ blocks. The long lifetimes of these resonance states are a reflection of how well the $K$ quantum numbers are defined in ArHCl. Since the Coriolis coupling induces interaction between $K$ blocks which differ by $\Delta K=\pm 1$, the resonance states mainly decay into HCl ($J=K-1$) rotational state if it is open. Thus, the decay probabilities into lower $J$ states are relatively small for a given resonance state.

The interaction anisotropy, however, decreases as $R$ increases. As the system approaches the free-rotor limit, the isotropic contribution becomes more dominant. In this limit, $J$ is a good quantum number. A given $J$ state may still support positive energy bound states which become resonance states as a result of mixing with unbound (or scattering) states of lower $J$ levels. The stronger the mixing among different $J$ states, the shorter the lifetimes of resonance states would be. The $J$ mixing is primarily induced by the interaction anisotropy. Many short-lived resonance states, that are given in Table IV, may result from this mechanism. Additional analysis of resonance features may be found in the work of Ashton et al. (Ref. 16).

At this point, critical comments and evaluation of the search algorithm in the present form may be made. Note that the problems are not with the calculations of $S$ and $Q$ but with the assignments of isolated resonance parameters. First, the parameters for resonance states located just above a threshold energy may not be accurately calculated because of the highly nonconstant background effect and/or the limitation of the averaging process in that energy region. A more accurate result may be obtained if nonlinear least-squares fits are made to Eq. (17) with polynomial expansions of $Q_0(E)$. Second, the existence of overlapping resonances along with nonconstant $Q_0$ introduces additional errors in $\tilde{E}_R, \Gamma$, and $\Gamma_I$. However, the background effect is negligible for long-lived resonance states ($>1$ ns) whether it is constant or not as demonstrated in Fig. 2. To treat these overlapping resonances properly, multilevel $S$ matrix partition may be adopted. Third, it is observed that the search algorithm may occasionally miss broad resonances especially when the background $Q_0(E)$ is significantly varying across the resonance and/or if they are almost overlapped to other resonances. It becomes, however, a matter of semantics whether these are just scattering states or resonances. Consequently, the resonance states listed in Tables III and IV are not meant to be exclusive, since broad shape resonances which lie just above threshold may be missing as indicated by the absence of $0.163 \ cm^{-1}$ resonance of $J=10, p=0$ in the present calculations. Fourth, a special precaution may have to be taken for an extremely narrow resonance, since its position is likely to be extremely close to the corresponding discrete eigenvalue of $H$, and this may cause overflow error in the Green's function of Eqs. (11) and (12). However, no prac...
### TABLE III. Positions and lifetimes of long-lived resonance states for $J=0,1$, and 10.

<table>
<thead>
<tr>
<th>$E_R$ (cm$^{-1}$)</th>
<th>$\tau$ (basis S) (ns)$^a$</th>
<th>$\tau$ (basis T) (ns)</th>
<th>$\tau$ (basis L) (ns)</th>
<th>$E_R$ (cm$^{-1}$)</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(J=0, p=0)$</td>
<td>$(J=1, p=0)$</td>
<td>$(J=10, p=0)$</td>
<td></td>
<td>$(J=0, J=1, J=10)$</td>
</tr>
<tr>
<td>12.491</td>
<td>0.44</td>
<td>0.4563</td>
<td>0.4586</td>
<td>0.777</td>
<td>100</td>
</tr>
<tr>
<td>17.081</td>
<td>0.18</td>
<td>0.1893</td>
<td>0.1884</td>
<td>3.664</td>
<td>100</td>
</tr>
<tr>
<td>19.696</td>
<td>0.11</td>
<td>0.1119</td>
<td>0.1115</td>
<td>10.702</td>
<td>100</td>
</tr>
<tr>
<td>20.740</td>
<td>0.27</td>
<td>0.2531</td>
<td>0.2524</td>
<td>12.556</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$(J=1, p=1)$</td>
<td></td>
<td></td>
<td></td>
<td>$(J=0, J=1, J=10)$</td>
</tr>
<tr>
<td>0.777</td>
<td>8.3</td>
<td>8.3</td>
<td>8.3</td>
<td>0.4586</td>
<td></td>
</tr>
<tr>
<td>3.664</td>
<td>1.97</td>
<td>1.977</td>
<td>1.977</td>
<td>0.1884</td>
<td></td>
</tr>
<tr>
<td>10.702</td>
<td>2.3</td>
<td>2.310</td>
<td>2.310</td>
<td>10.703</td>
<td></td>
</tr>
<tr>
<td>12.556</td>
<td>0.46</td>
<td>0.4272</td>
<td>0.4735</td>
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<td></td>
</tr>
<tr>
<td>16.602</td>
<td>5.7</td>
<td>5.797</td>
<td>5.814</td>
<td>16.602</td>
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</tr>
<tr>
<td>17.136</td>
<td>0.15</td>
<td>0.1894</td>
<td>0.1839</td>
<td>18.095</td>
<td></td>
</tr>
<tr>
<td>19.544</td>
<td>7.1</td>
<td>7.140</td>
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<td>19.545</td>
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</tr>
<tr>
<td>19.738</td>
<td>0.11</td>
<td>0.1160</td>
<td>0.1156</td>
<td>19.783</td>
<td></td>
</tr>
<tr>
<td>20.700</td>
<td>2.6</td>
<td>2.501</td>
<td>2.492</td>
<td>20.695</td>
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</tr>
<tr>
<td>20.768</td>
<td>0.32</td>
<td>0.2957</td>
<td>0.2950</td>
<td>20.768</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(J=1, p=0)$</td>
<td></td>
<td></td>
<td></td>
<td>$(J=0, J=1, J=10)$</td>
</tr>
<tr>
<td>0.777</td>
<td>100</td>
<td></td>
<td></td>
<td>0.163</td>
<td></td>
</tr>
<tr>
<td>3.664</td>
<td>100</td>
<td></td>
<td></td>
<td>5.176</td>
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</tr>
<tr>
<td>10.702</td>
<td>100</td>
<td></td>
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<td>8.915</td>
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<td>12.556</td>
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<td>17.136</td>
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<tr>
<td>19.544</td>
<td>100</td>
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<td>18.095</td>
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<tr>
<td>19.738</td>
<td>100</td>
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<td>19.545</td>
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<td>20.700</td>
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</tr>
<tr>
<td>20.768</td>
<td>100</td>
<td></td>
<td></td>
<td>20.768</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(J=10, p=0)$</td>
<td></td>
<td></td>
<td></td>
<td>$(J=0, J=1, J=10)$</td>
</tr>
<tr>
<td>0.4586</td>
<td></td>
<td></td>
<td></td>
<td>0.1884</td>
<td></td>
</tr>
<tr>
<td>1.884</td>
<td></td>
<td></td>
<td></td>
<td>0.1115</td>
<td></td>
</tr>
<tr>
<td>0.2524</td>
<td></td>
<td></td>
<td></td>
<td>0.4586</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Summary of three basis sets calculations as in Table II with $R_f=16.0$ Å.

$^b$Flux-operator method results of Ref. 17. Results are semiquantitative.

$^c$Present results, each probability is sum of $\Gamma_j/\Gamma$ for the same $j$ states [where $i=(j,f)$ asymptotic channel]. The listed values are converged at least for two calculations unless otherwise noted.

$^d$Converged at least for two calculations. Uncertainty is from 0 to ±9 in the last digit.

$^e$%=$\Delta P$, same for other present results entries. Uncertainty is from 0 to ±9 in the last digit.

$^f$Basis S calculation results. Maximum difference between each probability of three calculations is 0.07.

V. CONCLUSION

Several recommendations guiding calculational parameters targeting specific concerns about resonance states may be obtained from the present calculations. Given a...
reflects the characteristics of these resonances. Regarding efficient for translationally compact Feshbach resonance saying that the discrete eigenvectors must be good approximations to the solutions of Schrödinger solution in the finite range. A relatively small basis set range is often sufficient for translationally compact Feshbach resonance states. On the other hand, a larger range is required for diffusive Feshbach or shape resonance states. This simply reflects the characteristics of these resonances. Regarding the kinds of translational basis functions, Sturmian functions are suitable for low to high energy resonance states with moderate accuracy, Lobatto shape functions are very accurate for low energy ones, and sine functions give high accuracy over the full energy range. These characteristics are largely determined from the distribution patterns of their respective quadrature points or nodal patterns. We note, however, that the sine and Lobatto shape function bases must be larger and take more CPU times as shown in Table V.

In this paper, the efficiency and accuracy of FRSW method is demonstrated for the problem of multiple resonance states search. In particular, many rotational resonances of Ar–HCl(\(v=0\)) are calculated efficiently via the lifetime matrix calculation. One portion of the computation, i.e., the diagonalization of Hamiltonian matrix is common to the bound state calculations. This makes the resonance state calculations a simple extension of the bound state calculations.

Since all the effective centrifugal potential terms (\(\propto 1/R^2\) which are long range than the van der Waals interaction potential) are included in the asymptotic Hamiltonian operator even in the present body-fixed frame representation, the translational dynamical range to consider is reduced to that required for the “real” interaction potential (see Ref. 27 for a different treatment).

A simple search algorithm to locate and calculate multiple resonance states is presented and applied. If we target, mainly, isolated, simple resonance states with almost constant background effects, for example, we find a maximum 67 resonance states for Ar–HCl in \(J=10\). Also, the numerically calculated lifetimes have, at best, qualitative agreement with the highly accurate results presented here.

The current approach, requiring only a single real diagonalization of the \(L^2\) basis, appears highly advantageous compared with stabilization, complex rotation/scaling, optical potential, and other scattering methods.
TABLE V. Successive diagonalization-truncation scheme and CPU times for J=10.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>SDT scheme</th>
<th>Discrete eigenvalues</th>
<th>Resonance states</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis S</td>
<td>60×10×5→450×5→</td>
<td>321 (\beta)</td>
<td>325</td>
<td>67</td>
</tr>
<tr>
<td>Basis T</td>
<td>100×10×5→700×5→</td>
<td>386 (\beta)</td>
<td>390</td>
<td>66</td>
</tr>
<tr>
<td>Basis L</td>
<td>80×10×5→650×5→</td>
<td>386 (\beta)</td>
<td>390</td>
<td>24</td>
</tr>
</tbody>
</table>

*aAs in Table II.
*bSize of direct product basis set at each stage of SDT, see Ref. 17 for details.
*cNumber of discrete eigenvalues of Hamiltonian matrix of Eq. (6) scanned.
*dNumber of resonance states found.
*eCPU time on Stardent GS2000 computer for each calculation. It is partitioned to 622 for matrix diagonalization, 384 for integral evaluations, 1174 for resonance search for basis S calculation, for example.
*f\(p\)=0 state, same for other entries.
*g\(p\)=1 state, same for other entries.

ACKNOWLEDGMENTS

H.W.J. thanks Dr. O. A. Sharaffedin for helpful discussions about the asymptotic eigenfunctions in body-fixed frame. We thank the referee for pointing out the work of Ashton et al. We acknowledge the support of the National Science Foundation Grant No. NSF-CHE-9307792.

APPENDIX: BOUNDARY EFFECT ON \(\text{Tr } Q\)

Here, we consider explanations for the fact that the FRSW must be evaluated for some distance from the outer boundary of the translational basis set range in order to obtain accurate \(\text{Tr } Q\) in the SDT scheme. To simplify the argument, a one-dimensional system is considered. The unnormalized FRSW is expanded in a finite basis set, \(\{\phi(R)\}\), on \(R\in[0,\infty]\) satisfying the usual zero boundary conditions plus a linear auxiliary function, \(f(R)\). It is given by

\[
|\Psi(\alpha)\rangle = \sum_{\alpha=1}^{N} |\alpha\rangle \langle (E-\hat{H})^{-1}|\beta\rangle \langle \hat{H} - E | f\rangle + |f\rangle, 
\]

(A1)

where

\[
|\Psi(0)\rangle = |f(0)\rangle, \quad |\Psi(S)\rangle = |f(S)\rangle, 
\]

and \(\{\alpha\}\) are the finite representation in which \(\hat{H}\) may be diagonalized. Then, since,

\[
\langle \gamma | (\hat{H} - E) |\Psi\rangle = 0, \quad \gamma \in \{\alpha\}, \quad (A2) 
\]

is satisfied exactly, if \((\hat{H} - E) |\Psi\rangle\) is exclusively expandable by \(\{\alpha\}\) inside the range defined, this \(|\Psi\rangle\) is the desired nontrivial eigenfunction of the Schrödinger equation. If \((\hat{H} - E) |\Psi\rangle\) is rearranged as

\[
(\hat{H} - E) |\Psi\rangle = \sum_{\alpha=1}^{N} |\alpha\rangle \cdot s - E \sum_{\alpha=1}^{N} |\alpha\rangle \cdot s + \hat{H} | f\rangle \quad - E |f\rangle , 
\]

(A3)

where

\[
s = \sum_{\beta=1}^{N} \langle \alpha | (E-\hat{H})^{-1}|\beta\rangle \langle \beta | \hat{H} - E | f\rangle , 
\]

then, judging from the partitioning of terms, it is noticed that a sufficient condition of the exclusive expandability of \((\hat{H} - E) |\Psi\rangle\) by \(\{\alpha\}\) is that all \(|\alpha\rangle\)'s, \(|f\rangle\), and \(\hat{H} | f\rangle\) be eigenfunctions of \(\hat{H}\) and, at the same time, be expandable by \(\{\alpha\}\).

The SDT scheme generates approximate eigenfunctions corresponding to \(\{\alpha\}\); however, no special attention is given to incorporate the components of \(|f\rangle\) and \(\hat{H} | f\rangle\). In particular, \(|f\rangle\) may be poorly expanded by such basis set since it is nearly increasing to the outer boundary while the basis functions go to zero there and, in the SDT scheme, we retain the lower energy states which vary more slowly near the boundary. As a result, the Schrödinger equation with the unnormalized FRSW as a trial solution may be less satisfied close to the outer boundary. This argument provides the possible reason why \(\text{Tr } Q\) deviates from the ideal damping oscillation close to the outer boundary as in Fig. 1.