Concluding Remarks

This paper addresses the questions we raised about dephasing and vibrational energy redistribution in small and large molecules. We outlined the laser techniques that can be used to probe these dynamical processes. The relavance of optical T_1 and T_2 to selectivity is emphasized; the success of laser-selective chemistry must depend on knowledge of the time scales for irreversible vibrational redistribution and the loss of phase coherence. As evident from the anthracene (isolated molecule) results, these time scales depend on the excess energy in the molecule and the degree of internal cooling.

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(28) Further recent experiments have revealed a dependence of the beat pattern as well as the modulation amplitude upon the pressure and nature of the carrier gas. These results and their interpretation will be discussed in a forthcoming paper.

Resonance Energies and Lifetimes from Stabilization-Based Methods

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A practical, computationally simple procedure is presented for calculating energies and widths of resonances in atom–diatom complexes. It combines the stabilization method and a "golden rule" formula, employing only square-integrable basis functions. The utility of the procedure is tested on rotationally predissociating model atom–diatom van der Waals complexes. In addition, a procedure for performing coordinate rotation in small, selected subspaces of stabilization eigenvectors is proposed and applied to a two-open-channel model potential problem. A perturbation-based scheme is developed for systematic selection of those stabilization eigenvectors which should be included in the subspace.

Introduction

In low-energy atom (molecule)–molecule collisions, part of the relative kinetic energy of motion may be temporarily converted into excitation of the internal (rotational and/or vibrational) degrees of freedom of either partner. For sufficiently attractive interactions, the additional kinetic energy gained may enable states otherwise energetically inaccessible to be excited. When this excitation occurs, the atom–excited molecule system has insufficient energy, in its relative motion, to separate. The transient complex thus formed is referred to as a Feshbach or compound-state resonance. Eventually, the internal energy is transferred back into the relative translational energy, leading to breakup of the complex. Hence, these resonances correspond to predissociating, metastable states characterized by total energies, E_r, and widths, Γ_r, the latter being related to the lifetime τ by the uncertainty relationship $\tau = \hbar/\Gamma$. Another class of resonances are the orbiting or shape resonances in which the colliding partners are temporarily held together by a centrifugal barrier. Literature devoted to theoretical and experimental investigations of both kinds of resonance states is extensive and has been summarized recently in two articles by Toennies and his collaborators.[1,2]

In a time-dependent picture, resonances can be viewed as localized wave packets made by superposition of continuum wave functions, which for a time $\tau = \hbar/\Gamma$ qualitatively resemble bound states.[3,4] During the time τ, the amplitude of the scattering wave function at a resonance energy is much larger in the region where the interaction potential is significant than in the asymptotic region. The localized nature of the resonance wave function has motivated the development of several purely L^2 methods for calculating resonance energies and widths. In such methods, scattering wave functions are expanded in terms of square-integrable basis functions. Here we can mention the secular equation method of Grabenstetter and Le Roy,[5] the complex coordinate rotation method,[6] the stabilization method pioneered by Hazi and Taylor[3] (on which we focus our attention in this article), and the closely related truncated orthogonalization procedure of Holøien and Midtal.[7]

In the stabilization method[3,8,9] the wave function is expanded in a square-integrable basis and a finite dimensional matrix representation of the relevant Hamiltonian is constructed. The resonance eigenvalues (one or more) are identified as those which are "stable" (relatively insensitive) to variations of the basis, such as increasing the

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[*] Camille and Henry Dreyfus Fellow, John Simon Guggenheim Fellow.

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size of the basis[3] or scaling of the spatial size of the basis functions. From a so-called stabilization graph the resonance energy can be estimated directly. Hazi and Taylor,[3] Fels and Hazi,[10-12] and Hazi[13] have demonstrated that resonance widths can also be extracted from stabilization calculations. These methods have been applied to one-dimensional model problems[3,10-12] and autoionizing electronic states of atoms[13,14] and H_2^-.[15]

In section II we outline a procedure in which energies of resonances (predissociating, metastable states) in atom–diatom systems can be determined using the stabilization method. The resonance widths are then calculated by employing the "golden rule" formula of Miller, the use of which has thus far been restricted to one-dimensional model problems,[10-12] autoionizing states of atoms,[16-18] and Penning ionization.[19] The necessary resonances and continuum wave functions are approximated by the appropriate eigenvectors obtained from the stabilization procedure, very much in the spirit of the paper by Hickman, Isaacson, and Miller on autoionizing states of He and H^-.[16] Thus, the method proposed here also involves expansion in terms of L^2 basis functions. However, in contrast to the coordinate rotation-based methods, which have been applied to similar problems,[20,21] it involves only real arithmetic; diagonalizations of complex matrices, performed repeatedly during the search for resonances in the complex plane, are avoided completely. The resulting reduction in computation time is very significant.

The stabilization-golden rule procedure outlined above, although computationally simple and fast, has certain drawbacks. Determination of resonance energies via the stabilization calculation becomes less accurate for broader resonances. Miller's golden rule expression[16-19] for resonance widths can, in its present form, be readily applied only to one-open-channel problems. On the other hand, the coordinate rotation (CR) method[6] is very general, capable of treating many-open-channel resonances in diverse atomic and molecular systems. Yet, the dimensionality of the complex symmetric matrix to be diagonalized repeatedly grows very rapidly with the inclusion of additional channels thus making the search for resonances prohibitively time consuming and expensive. One possible solution to this problem is developed in section IV. There, we combine the stabilization and coordinate rotation (CR) methods; the complex scaled Hamiltonian is repeatedly diagonalized (in the course of performing a so-called θ trajectory) in a *small, selected subspace* of eigenvectors resulting from a previous stabilization calculation. In other words, we suggest that CR calculations be performed within selected subspaces of stabilization eigenvectors as basis sets, thus substantially reducing the dimensionality of the problem and, therefore, the computation time and cost. A perturbation-based scheme is developed for the systematic selection of those stabilization eigenvectors which should be included in the subspace.

In section II we describe the stabilization method and Miller's golden rule formula as it is utilized in this work. Also in section II, the Hamiltonian is defined for the five model atom–diatom van der Waals systems on which the procedure is tested. In section III, the results of our calculations using the stabilization-golden rule method are presented and compared with those obtained previously using other methods. In section IV, the method of coordinate rotation in selected stabilization eigenvector subspaces is analyzed in terms of a simple two-open-channel model. Section V contains some concluding remarks.

II. Stabilization Method and Miller's "Golden Rule" Formula

In the Holøien–Midtal version[7] of the stabilization method, the real eigenvalues E of the Hamiltonian are computed as a function of the scale parameter α, the resonance positions E_r being characterized by the condition[22]

$$(\mathrm{d}E/\mathrm{d}\alpha)_{\alpha_{\mathrm{opt}}} \approx 0 \tag{1}$$

We have applied their procedure to five model atom–diatom van der Waals (vdW) A–BC systems which have been previously studied by a variety of other methods. In this investigation we have chosen to scale the atom–diatom separation vector $\vec{r}$ as follows:

$$\vec{r} \rightarrow \alpha\vec{r} \tag{2}$$

where α is a real number. This could, alternatively, be viewed as a scaling of the L^2 basis functions used to expand the r dependence of the wave functions. The resulting scaled Hamiltonian for the model atom–diatom (rigid rotor) systems is

$$H(\vec{R},\alpha\vec{r},\theta) = -\alpha^{-2}\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{l^2}{r^2}\right] + B_{\mathrm{d}}j^2 + V(\alpha r,\theta) \tag{3}$$

where μ is the reduced mass of the system $(m_Am_{BC}/(m_A + m_{BC}))$, θ is the angle between the diatom's orientation vector $\vec{R}$ and the atom–diatom separation vector $\vec{r}$, l^2 is the square of the angular momentum operator associated with rotation of the atom A about the molecule BC, j^2 is the square of the angular momentum operator associated with rotation of BC, and B_d is the rotational constant for BC (treated as a rigid rotor). The interaction potential V is written in the form

$$V(r,\theta) = V_0(r) + V_2(r)P_2(\cos\theta) \tag{4}$$

where both V_0 and V_2 are (modified) Lennard-Jones functions. The basis in terms of which the radial (r) wave function is expanded consists of the product of free-rotor states and, in the present work, Gaussian basis functions whose centers span at least the region of r space where V is significant. All of the parameters necessary to specify the model problems and the basis set are given in section III.

For a given value of α, a matrix representation of the scaled Hamiltonian, $H(\vec{R},\alpha\vec{r},\theta)$, is constructed in the basis described above. The resulting matrix has dimension $lN \times lN$, where N is the number of Gaussian basis functions, and l is the number of channels (open plus closed). Diagonalization of this matrix yields a set of lN eigenvalues and corresponding orthonormal eigenvectors. The diagonalization is repeated for various values of α. The eigenvalues are then plotted as functions of α to give the so-called stabilization graph. For each of the model problems,

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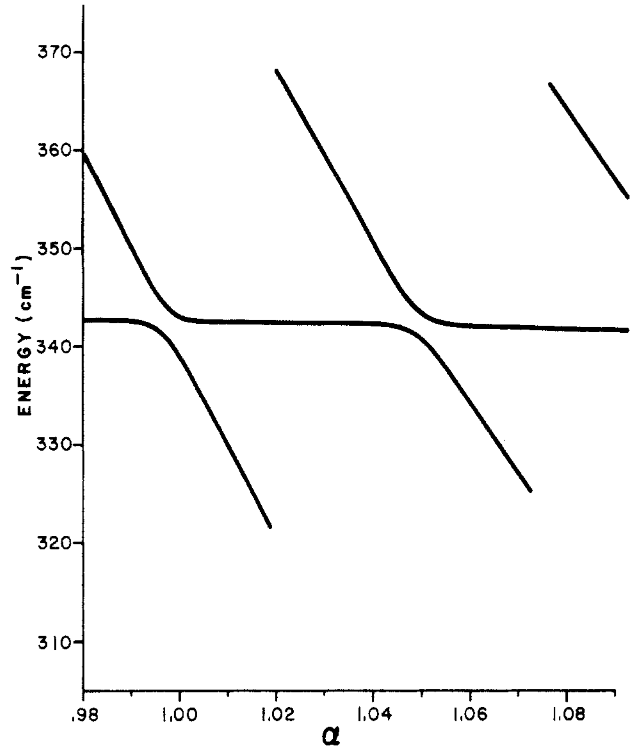

Figure 1. Stabilization graph for the metastable state in a one-open-channel atom–diatom van der Waals complex (system II, see section III). A series of avoided crossings represents a resonance at 344 cm^{-1}.

there is one eigenvalue which is, when compared to other eigenvalues, rather insensitive to the changes in α (Figure 1). As is discussed in section III, these "stable" eigenvalues are close to the resonance energies calculated by other methods for these same model problems. Figure 1 also shows that, at quite regular intervals, other continuum-like solutions descend toward, and eventually stabilize at, the resonance eigenvalue. Such behavior was noticed and very nicely analyzed years ago by Hazi and Taylor[3] (for the case of a one-dimensional model problem). This observation was also made in a paper by Greenawalt and Dickinson who treated bound and quasi-bound states of diatomic molecules.[23] The fact that, for certain values of the scaling parameters α, the resonance and continuum-like eigenvalues approach one another and undergo an "avoided crossing" is essential to the procedure described below for calculating resonance widths.

The "golden rule" expression, proposed for use in analogous electron-atom resonance problems by Miller some 15 years ago,[18] expresses the resonance width as

$$\Gamma = 2\pi\rho|\langle\psi_r|H - E_r|\chi_c\rangle|^2 = 2\pi\rho(E_c - E_r)^2|\langle\psi_r|\chi_c\rangle|^2 \qquad (5)$$

Here ψ_r is the resonance wave function, χ_c is a continuum wave function which is (ideally) degenerate with ψ_r, and ρ represents the density of (translational) continuum states at the kinetic energy of the A + BC translational motion. Following the proposal of Miller et al.,[16] we approximate ψ_r by the closed channel component (projection) of the "stable" resonance eigenvector obtained from the stabilization calculation. χ_c is approximated by the eigenvector corresponding to the descending continuum-like eigenvalue (see Figure 1), also obtained from the stabilization calculation. We stress that χ_c is not obtained by solving a separate scattering problem in which only open-channel functions are used; χ_c contains both open- and closed-channel pieces.

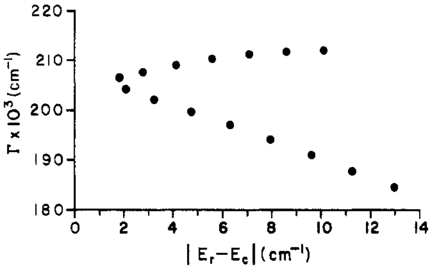

Figure 2. The resonance width Γ for the model atom–diatom system II (see section III), calculated by using the golden rule formula (eq 5) for several values of α, on both sides of the avoided crossing nearest to α = 1.

TABLE I: Parameters Characterizing the Model Atom-Diatom vdW Systems

	system I[a]	system II[a]	Ne-H$_2$[b]	Ar-H$_2$[b]	Kr-H$_2$[b]
μ, amu	1.9188	1.981	1.8328	1.9191	1.9686
B_d, cm^{-1}	60.0	60.551	60.0	60.0	60.0
ϵ, cm^{-1}	47.0	60.408	25.362	53.938	69.327
σ, Å	3.13685	3.4745	2.9426	3.2423	3.3925
a	0.13	0.09	0.1036	0.4184	0.1329
b	0.13	0.5	0.1488	0.1192	0.2370

[a] The interaction potential is described by eq 6 and 7.
[b] The interaction potential is described by eq 8 and 9.

If eq 5 is used in this manner and again following Miller's prescription, Γ is then determined for a number of values of α, for which the continuum-like (E_c) and resonance eigenvalues (E_r) are close. The result is finally extrapolated to $|E_r - E_c| = 0$. As is seen in Figure 2, this extrapolation is rather straightforward. However, one must, of course, avoid the region of α space where E_c and E_r do not vary linearly with α (i.e., near the avoided crossing). The density of continuum states ρ, which enters eq 5, is determined in the way described by Miller et al.,[16] which is based upon fitting the translational energy of the A + BC motion to a particle-in-a-box formula which, when the basis' radial extent is used to define the box length, gives the quantum number (and hence state density) corresponding to this translational energy.

III. Results of Calculations on Model Atom-Diatom van der Waals Systems

The above procedure, as already mentioned in section II, has been applied to five model van der Waals (vdW) atom–diatom (rigid rotor) A–BC systems. The Hamiltonian for all of the systems is given in eq 3. These model systems fall into two categories. In the first one are two weakly anisotropic systems previously treated, using other methods, by a number of workers.[5,24-26] Their interaction potential is $V(r,\theta) = V_0(r) + V_2(r)P_2(\cos\theta)$, eq 4), where

$$V_0(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \qquad (6)$$

$$V_2(r) = 4\epsilon[b(\sigma/r)^{12} - a(\sigma/r)^6] \qquad (7)$$

The values of all of the parameters necessary to specify the two model systems are given in Table I. Only a single metastable Feshbach state correlating with the isotropic closed channel ($j = l = 2$, $J = 0$) is considered here. Thus, the single open channel of these two (homonuclear) model

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TABLE II: Comparison of One-Open-Channel ($j = 2$) Resonance Energies and Widths for the Atom-Diatom Systems I and II Calculated in Various Ways

	system I		system II	
	E_r, cm^{-1}	Γ, cm^{-1}	E_r, cm^{-1}	Γ, cm^{-1}
S-M[a]	349 (±1)	1.4 (±0.1) × 10^{-2}	344 (±1)	0.20 (±0.01)
SE[b]	342.80 (±0.001)	1.1 (±0.1) × 10^{-2}	338.13 (±0.01)	0.16 (±0.01)
CCS[c]	342.81	1.0 × 10^{-2}	338.124	0.11
CC[d,g]	342.806			
A[e,g]			338	0.11
D[f,g]				

[a] Stabilization–Miller's "golden rule" formula; present work. [b] Secular equation method of ref 5. [c] Numerical solution of coupled equations with Siegert boundary conditions imposed, ref 24. [d] Numerical solution of coupled equations. [e] Adiabatic decoupling approximation of ref 28. [f] Distortion decoupling approximation of ref 28. [g] Data and original references quoted in ref 5.

problems has $l = j = J = 0$. The quantum numbers j and l refer to the rotation of $\vec{R}$ and $\vec{r}$, respectively, and J refers to the total angular momentum of the triatomic system. The angular basis is restricted to $l, j \leq 2$, and $J = M = 0$. To expand the radial wave functions, sets of Gaussian basis functions are used, with exponents equal to 20. These exponents were chosen so that neighboring Gaussian functions would have appreciable (≈25%) overlap. The centers of the Gaussian functions are given by

$$r_m = 3.0 + m \times 0.372 \text{ Å} \qquad (0 \leq m \leq N) \text{ for system I}$$

$$r_m = 3.3 + m \times 0.372 \text{ Å} \qquad (0 \leq m \leq N) \text{ for system II}$$

N, the number of Gaussian basis functions, was increased from 15 to 40 in our calculations so that we could monitor the convergence of the results. The Gaussian centers r_m were chosen so as to span the region of r space where V is significant. The left-most Gaussian was placed somewhat inside the classical turning point of the A + BC collision (as determined via V_0). The next (and all subsequent) Gaussian was then placed so that the spacing between neighboring functions was less than one-half the de Broglie wavelength expected for the open-channel-function.

In the second category are three van der Waals molecules X–H_2 (X ≡ Ne, Ar, Kr) previously treated by Beswick and Requena.[27] These authors expressed $V_0(r)$ and $V_2(r)$ in terms of Morse potentials. These potentials are not homogeneous which makes them somewhat inconvenient for use in our method (the matrix elements of the Hamiltonian would explicitly depend on α and would have to be recalculated at each point of the stabilization trajectory). We therefore chose to fit the Morse potentials of ref 27 to our own Lennard-Jones-like potentials

$$V_0(r) = \frac{27}{4}\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{8}\right] \qquad (8)$$

$$V_2(r) = \frac{27}{4}\epsilon\left[b\left(\frac{\sigma}{r}\right)^{12} - a\left(\frac{\sigma}{r}\right)^{8}\right] \qquad (9)$$

The conspicuous coefficient 27/4 in eq 8 and 9 is needed if one wants the depth of the potential $V_0(r)$ at its equilibrium position, $r_{eq} = (3/2)^{1/4}\sigma$, to be ϵ. The parameters σ, a, and b were determined by using a linear least-squares fitting program. We have found these Lennard-Jones (LJ) 12–8 potentials capable of reproducing the Morse potentials very well (certainly much better than the standard LJ 12–6 potentials, which we have also tried). All of the parameters necessary to specify the LJ 12–8 potentials (eq 8 and 9) are given in Table I.

Beswick and Requena[27] calculated the resonance energies and widths in the X–H_2 molecules mentioned above for several values of the rotational quantum number j(j = 2, 4, 6) of H_2, thus providing an excellent additional opportunity to check our method. For these molecules we could investigate the metastable Feshbach states correlating with the isotropic closed ($j = l = 2$, $J = 0$) and ($j = l = 4$, $J = 0$) channels. The latter state has two open channels, ($j = l = 2$, $J = 0$) and ($j = l = 0$, $J = 0$). For the radial wave function expansion, we again used Gaussian basis sets with exponents equal to 20.0. The centers of these Gaussians are given by

$$r_m = 2.5 + m \times 0.372 \text{ Å} \qquad (0 \leq m \leq N) \text{ for Ne–H}_2$$

$$r_m = 2.8 + m \times 0.372 \text{ Å} \qquad (0 \leq m \leq N) \text{ for Ar–H}_2$$

$$r_m = 3.0 + m \times 0.372 \text{ Å} \qquad (0 \leq m \leq N) \text{ for Kr–H}_2$$

with N ranging from 18 to 40. The reasons for choosing this particular set of parameters, i.e., $\{\alpha, r_m\}$, have already been given in connection to the basis set choice for systems I and II (this section).

TABLE III: Comparison of Resonance Energies and Widths for X-H_2 (X ≡ Ne, Ar, Kr) vdW Molecules

	E_r, cm^{-1}		Γ, cm^{-1}	
j	stabilization[a]	Beswick[b]	golden rule[a]	Beswick[b]
		Ne–H_2		
2	364.1	364.5	7.2 × 10^{-3}	5.1 × 10^{-3}
4	1220.8	1224.2		0.14 × 10^{-3}
		Ar–H_2		
2	347.4	347.2	1.76 × 10^{-2}	0.77 × 10^{-2}
4	1200.7	1206.6		0.36 × 10^{-3}
		Kr-H_2		
2	335	339	0.039	0.012
4	1192.6	1197.8		0.97 × 10^{-3}

[a] Stabilization–Miller's "golden rule" formula; present work. [b] Beswick and Requena, ref 27.

Resonance energies were determined from the stabilization graphs (e.g., Figure 1). The precision of the estimates depends on the "stability" of the resonance eigenvalue which, in turn, depends on the width of the resonances. The narrower the resonance the greater is the stability of its eigenvalue. This observation was made long ago by Hazi and Taylor.[3] Narrow resonances are also more suitable for determination of widths using our procedure since their "stable", linear stabilization graphs facilitate the extrapolation involved in calculation of the widths via Miller's golden rule formula (eq 5). The resonance energies and widths of the vdW systems studied in this work are listed in Tables II and III. We see that energies of both one (j = 2)- and two (j = 4)-open-channel resonances

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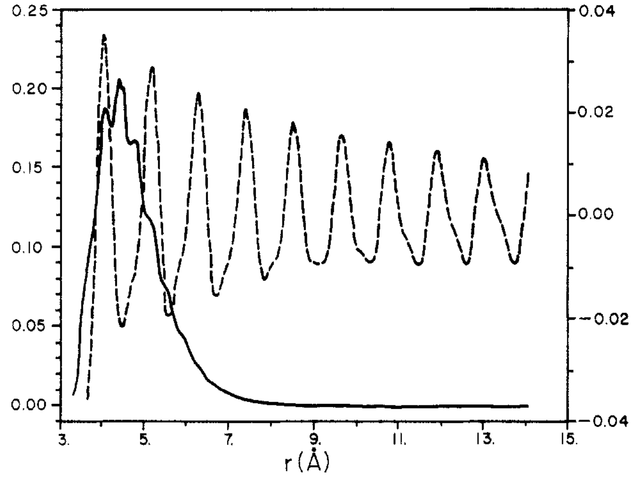

Figure 3. Model atom–diatom system II, for $N = 30$ and $\alpha = 0.97$. Open (- - -; left-hand-side scale) and closed (—; right-hand-side scale) channel components of the resonance radial wave function.

calculated by stabilization agree well with those obtained by other methods. These results lend support to the statement that stabilization can, in a computationally simple way, give accurate positions of one- or many-open-channel resonances, particularly narrower ones in triatomic systems. One-open-channel resonance widths, obtained by using the golden rule formula (eq 5) (the golden rule expression, in its present form is inapplicable to many-open-channel cases), agree to within a factor $2 \sim 3$ (at worst) with the widths calculated by using other methods. This is, in our opinion, satisfactory, especially in view of the relative simplicity of the procedure.

It is of some interest to briefly discuss the qualitative features of the radial wave functions resulting from our stabilization calculations. The open- and closed-channel components of the resonance radial wave function for system II (which is typical of the other systems studied) are plotted in Figure 3. We see that the closed ($j = l = 2$, $J = 0$)-channel component of the radial wave function is very strongly localized in the region of the potential "well" (for system II, $V_0(r)$ has its minimum at 3.9 Å). In this inner region its amplitude is much larger than the amplitude of the open ($j = l = 0$, $J = 0$)-channel radial wave function. This corresponds nicely to the physical picture of the Feshbach resonance involved: an "almost bound" state with the rotor BC excited to $j = 2$ state and an atom A temporarily "trapped" (and thus localized) inside the potential well. The open-channel radial wave function exhibits the expected oscillatory behavior; it even has the expected de Broglie wavelength.

IV. Coordinate Rotation in the Stabilization Eigenvector Subspace

In the coordinate rotation (CR) method,[6] the dissociating coordinate $\vec{r}$ is subjected to the *complex* scaling transformation

$$\vec{r} \rightarrow \alpha\vec{r}e^{i\theta} \equiv \eta\vec{r} \qquad (\eta = \alpha e^{i\theta}) \tag{10}$$

The spectrum of the scaled Hamiltonian $H(\eta)$ contains a complex resonance (one or more) eigenvalue E ($= E_r - i\Gamma/2$) which, for angles beyond a certain critical value θ_c and for certain values of α, is independent of η[6,22]

$$(\mathrm{d}E/\mathrm{d}\eta) = (\mathrm{d}^2E/\mathrm{d}\eta^2) = \cdots = 0 \tag{11}$$

Also, for $\theta > \theta_c$, the resonance wave function is square integrable. In actual calculations, using a finite set of L^2 basis functions, one tries to satisfy the first of the conditions in eq 11

$$(\mathrm{d}E/\mathrm{d}\eta)_{\eta_0} = 0 \tag{12}$$

where $\eta_0 = \alpha_0 \exp(i\theta_0)$ is the optimal scale factor.[22] The resonance condition (eq 1) of the Holøien–Midtal stabilization procedure[7]

$$(\mathrm{d}E/\mathrm{d}\alpha)_{\alpha_{\mathrm{opt}}} \approx 0 \tag{13}$$

can actually be viewed as an approximation to eq 12, for $\theta = 0$. Another fact pointing at the close relation between the CR and stabilization methods is the observation that for successful location of resonances via complex scaling it seems to be absolutely essential to choose α (in eq 10) in the immediate vicinity of the avoided crossing (in fact, usually from the crossing nearest to $\alpha = 1$) in the α (or stabilization) trajectory.[24,30] Also, the resonance energy determined by the subsequent CR calculation usually differs very little from the energy estimated from the stabilization graph.[29,30]

It therefore appears plausible that, having determined the resonance energy via stabilization, it should be possible to calculate the width with less than a complete, full-scale coordinate rotation (CR) calculation. One idea suggests itself quite naturally. First, the stabilization calculation (α trajectory) should be performed, thereby locating an avoided crossing in the α trajectory (and simultaneously identifying the resonance state(s)). Then, for α within the neighborhood of the avoided crossing, a θ trajectory (a series of complex diagonalizations of $\mathbf{H}(\theta)$) should be done, but in a smaller, *selected subspace* of the stabilization eigenvectors which includes the resonance state (eigenvector) and other "important" eigenvectors whose selection is discussed below. The rest of the spectrum, i.e., the remaining stabilization eigenvectors, which are not as "important", could then be taken into account, if necessary by (hopefully) low-order perturbation theory. The idea we have just outlined has, in its basic elements, been proposed first by Winkler and Yaris[31] and Winkler.[32] However, they did not mention stabilization and stabilization eigenvectors at all. They speak in terms of (pseudo) eigenstates of $\mathbf{H}(0)$ (i.e., of the unrotated Hamiltonian) and a state which will become the resonance state upon appropriate rotation. It is not clear how they distinguish that particular state among all of the others (which is essential for selection of the "important" subspace) without performing the stabilization or a similar calculation.

We therefore decided to further explore the possibility of doing CR calculations using selected subspaces of stabilization eigenvectors as basis sets, with aim to significantly reduce the dimensionality of the problems and, hence, the computation time and cost. As an integral part of this effort, a perturbation-based scheme was developed to permit the systematic selection of those stabilization eigenvectors which sould be included in the subspace.

We tested the idea outlined above on a model two-open-channel problem previously used by Noro and Taylor[33] and Bačić and Simons[29] in their studies on CR calculations of branching ratios. In that case, both the stabilization and CR methods proved very successful in calculating the resonance parameters; thus the model seemed suitable for our purpose. The model Hamiltonian is (in atomic units)[33]

$$H = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + H_0(x) + V(x,r) \tag{14}$$

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(30) Z. Bačić, Ph.D. Thesis, University of Utah, 1981.
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(32) P. Winkler, *J. Phys. A*, **283**, 149 (1977).
(33) T. Noro and H. S. Taylor, *J. Phys. B*, 13, L377 (1980).

TABLE IV: Eigenvalues of $H(\alpha)$ ($\alpha = 1, \theta = 0$)

n	E_n	n	E_n
1	−2.314 271 304 037 32	19	11.133 630 465 733 03
2	−1.310 073 915 733 37	20	11.212 647 113 196 75
3	−0.537 258 889 746 67	21	13.941 303 807 802 51
4	−0.031 962 419 580 11	22	16.779 513 035 302 88
5	0.419 778 960 165 17	23	17.736 191 714 492 20
6	0.817 397 093 137 09	24	23.048 508 597 900 58
7	1.079 924 868 152 32	25	25.482 017 323 217 62
8	1.895 866 485 926 64	26	30.998 125 085 083 66
9	1.997 886 132 935 71	27	39.883 354 472 169 25
10	3.252 783 698 990 58	28	44.185 939 157 597 16
11	3.275 618 722 388 12	29	66.106 274 509 650 16
12	4.764 924 820 855 64	30	69.015 005 428 989 73
13	4.867 090 923 401 42	31	122.143 202 116 384 13
14	5.009 561 296 869 77	32	123.854 187 851 620 18
15	6.419 099 242 275 16	33	281.286 076 644 219 35
16	7.519 821 154 188 84	34	282.231 675 159 305 71
17	7.558 043 504 364 84	35	1 139.139 386 726 710 67
18	9.029 909 121 361 47	36	1 139.739 659 021 877 82

where H_0 is a target Hamiltonian defined to have two eigenstates

$$H_0(x)\phi_\alpha(x) = E_\alpha\phi_\alpha(x) \qquad \alpha = 1, 2 \tag{15}$$

The matrix elements of the interaction potential between target eigenstates are defined as follows:[33]

$$U_{\alpha\beta}(r) = \int \mathrm{d}x\ \phi_\alpha^*(x)V(x,r)\phi_\beta(x) = U_{\alpha\beta}r^2e^{-r} \tag{16}$$

$$\mathrm{U} = \begin{pmatrix} -1.0 & -7.5 \\ -7.5 & 7.5 \end{pmatrix}$$

The energies (E_α) of the target states are 0.0 and 0.1. A Slater-type orbital basis set was chosen[33] for the expansion of the r dependence of the CR wave function

$$\psi_\theta(x,r) = \sum_{\alpha j} C_j^{\alpha}\phi_\alpha(x)r^je^{-\xi r} \qquad \alpha = 1, 2;\ j = 1, 2, ..., 18 \tag{17}$$

The eigenvalues $\{E_n\}$ of the (unrotated) Hamiltonian at the point of the stabilization trajectory characterized by $\alpha = 1$, in the vicinity of the avoided crossing (see Figure 4), are listed in Table IV. In this table, the resonance eigenvalue E_R (and the corresponding eigenvector), determined via stabilization, is numbered 12. The problem of selecting those continuum states (eigenvectors) which are to be included in the subspace in which the complex diagonalizations (θ trajectories) will be performed was approached via perturbation theory.

Due to the peculiar form of the interaction potential matrix elements (eq 16), the Hamiltonian in eq 14 does not lend itself easily to factorization into some zeroth-order Hamiltonian and a perturbation, H'. Therefore, we decided to treat the coordinate rotation itself as a perturbation, i.e., to write

$$H(\eta) = H(\alpha) + [H(\eta) - H(\alpha)] \tag{18}$$

where $\eta = \alpha e^{i\theta}$ and $H(\alpha)$ is the nonrotated partially (real) scaled Hamiltonian. Then the perturbation term, $H'(\eta)$, is

$$H'(\eta) = H(\eta) - H(\alpha) \tag{19}$$

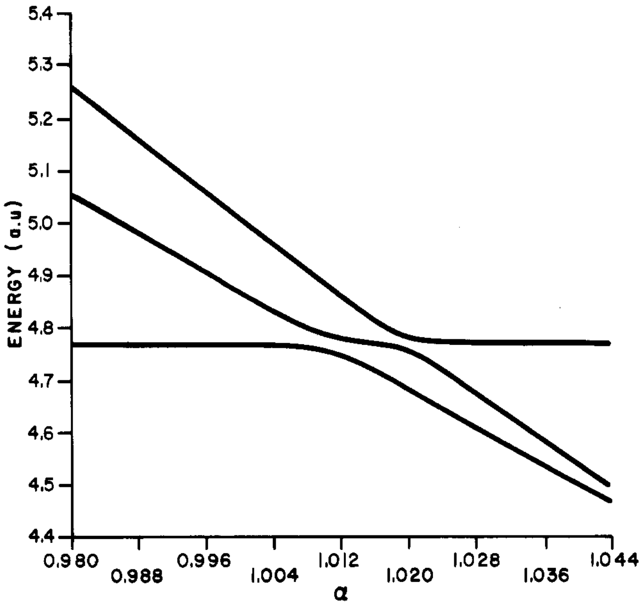

Figure 4. Stabilization graph for the resonance in the model two-open-channel potential problem.

The nondegenerate perturbation theory estimate of the second-order correction to the resonance energy E_R of the unrotated ($\theta = 0$) Hamiltonian can be written as

$$E_\mathrm{R}^{(2)}(\eta) = \sum_{n\neq \mathrm{R}}{}' \frac{\langle\Phi_\mathrm{R}|H'(\eta)|\Phi_n\rangle\langle\Phi_n|H'(\eta)|\Phi_\mathrm{R}\rangle}{E_\mathrm{R} - E_n} \tag{20}$$

where the Φ_n's and Φ_R (Φ_{12}) are the eigenvectors of $H(\alpha)$ (for $\alpha = 1$ in this case). Each of the terms in the summation in eq 20 is a complex number, for $\theta \neq 0$. Therefore, without going into much detail, we rewrite eq 20 in a rather symbolic form (since explicit working expressions are unimportant for our purposes) as

$$E_\mathrm{R}^{(2)}(\eta) = \sum_{n\neq \mathrm{R}}{}' \frac{\mathrm{Re}\ H'(\eta)_{\mathrm{R},n} + i\ \mathrm{Im}\ H'(\eta)_{\mathrm{R},n}}{E_\mathrm{R} - E_n} \tag{21}$$

where Re $H'(\eta)_{\mathrm{R},n}$ is the real part of $\langle\Phi_\mathrm{R}|H'(\eta)|\Phi_n\rangle\langle\Phi_n|H'(\eta)|\Phi_\mathrm{R}\rangle$, and Im $H'(\eta)_{\mathrm{R},n}$ stands for the imaginary part of the same expression. Defining

$$C(\eta)_{\mathrm{R},n} \equiv \frac{\mathrm{Re}\ H'(\eta)_{\mathrm{R},n} + i\ \mathrm{Im}\ H'(\eta)_{\mathrm{R},n}}{E_\mathrm{R} - E_n} \tag{22}$$

we may write eq 21 in the form

$$E_\mathrm{R}^{(2)}(\eta) = \sum_{n\neq \mathrm{R}}{}' C(\eta)_{\mathrm{R},n} \tag{23}$$

Although we and the others have looked into using such a second-order perturbation equation to actually compute resonance energies as the rotation is "turned on", it seems that such an approach is doomed to failure. The perturbation is simply too large. However, we do not intend to use eq 23 to evaluate the resonance energy and width. Rather, we are making use of the perturbation concept as a device to identify those eigenvectors which couple most strongly to our resonance eigenvector. These eigenvectors are then to be used in a matrix diagonalization (not perturbation) determination of the resonance parameters.

Since each (complex) term $C(\eta)_{\mathrm{R},n}$ in eq 23 contributes both to the resonance energy, through its real part, and to the resonance width, through its imaginary part, it seemed natural to take the magnitude of the modulus $|C(\eta)_{\mathrm{R},n}|$ (rather than the size of either Re $H'(\eta)_{\mathrm{R},n}$ or Im $H'(\eta)_{\mathrm{R},n}$ of eq 22 alone) as a measure of the coupling between the resonance state Φ_R and any of the other states Φ_n. The selection of the eigenvectors Φ_n to be included in the complex diagonalization subspace is thus based on the size of $|C(\eta)_{\mathrm{R},n}|$ (see Table V). The larger $|C(\eta)_{\mathrm{R},n}|$, the stronger the interaction between Φ_n and Φ_R, the more important that the state Φ_n should be included in the subspace. This gives our prescription for selecting the most important eigenvectors of $H(\alpha)$.

A glance at Table V reveals the somewhat disappointing fact that no *single* modulus $|C(\eta)_{\mathrm{R},n}|$ (or very small group of them) is overwhelmingly larger than the others. This

TABLE V: List of $|C^{(\eta)}{}_{\mathrm{R},n}|^a$

n	$\|C^{(\eta)}{}_{\mathrm{R},n}\|^a$	n	$\|C^{(\eta)}{}_{\mathrm{R},n}\|^a$
1	0.000 000 001 249 46	19	−0.000 209 221 222 66
2	0.000 000 044 079 05	20	−0.000 004 297 709 03
3	0.000 000 052 774 04	21	−0.000 000 002 105 88
4	0.000 000 043 222 22	22	−0.000 000 002 105 88
5	0.000 000 062 280 95	23	−0.000 022 616 142 73
6	0.000 000 023 182 37	24	−0.000 004 553 994 44
7	0.000 000 256 422 17	25	−0.000 000 001 085 82
8	0.000 000 348 348 77	26	−0.000 000 889 394 15
9	0.000 000 453 172 78	27	−0.000 000 000 222 91
10	0.000 000 674 626 09	28	−0.000 000 132 842 75
11	0.000 006 785 535 81	29	−0.000 000 000 170 11
12	0.000 000 000 000 00	30	−0.000 000 003 571 89
13	−0.009 153 599 158 26	31	−0.000 000 000 104 94
14	−0.000 363 732 235 44	32	−0.000 000 004 397 28
15	−0.000 200 241 352 92	33	−0.000 000 000 046 30
16	−0.000 007 239 306 78	34	−0.000 000 001 050 69
17	−0.000 555 684 613 44	35	−0.000 000 000 013 93
18	−0.000 414 232 208 06	36	−0.000 000 000 263 67

[a] Since the perturbation term $H'(\eta)$ (eq 19) vanishes for $\theta = 0$, the coupling elements $|C^{(\eta)}{}_{\mathrm{R},n}|$ were calculated for $\theta = 0.02$ rad ($\alpha = 1$). The choice of θ is quite arbitrary; the relative magnitudes of the coupling elements are constant over a wide range of the rotation angles θ.

means that there are a number of states (i.e., stabilization eigenvectors) which couple quite strongly to the resonance state (eigenvector number 12) and therefore have to be included in the subspace. However, since the time required to diagonalize a matrix varies as the third power of the matrix size, any appreciable fractional reduction in the number of eigenvectors which must be treated represents a substantial gain.

The observation that several eigenvectors interact strongly with Φ_R is in strong contrast with the case of ^{1}S resonance of He studied by Winkler and Yaris.[31] Through a similar analysis (although the Hamiltonian involved and the choice of its partitioning were very different from ours) they concluded that only two (pseudo) eigenstates of $\mathbf{H(0)}$ needed to be included into the subspace. Thus, the complex scaling calculation reduced essentially to repeated diagonalization of a 2 × 2 complex symmetric matrix, apparently yielding very good results.[31]

From Table V, it is evident that a group of states exists (numbers 11–23 (or 24)) whose coupling elements (i.e., the moduli $|C(\eta)_{\mathrm{R},n}|$) are by at least a factor of 5–10 larger than those of the others. If our concept of strength of interaction, or magnitude of coupling (measured by the size of $|C(\eta)_{\mathrm{R},n}|$) between the resonance and nonresonant states has some validity, complex scaling calculations in this subspace should give reasonable values for the resonance parameters. We see, from Table VI, that a coordinate rotation calculation including only the eigenvectors with numbers 11–24 reproduces the exact resonance energy (as determined by full CR calculation[29,33]) and a resonance width which differs by only 8.8% from the exact width. Such CRISES (coordinate rotation in the stabilization eigenvector subspace) calculations were performed for subspaces of varying dimensions; several of the results are shown in Table VI. It is clear that by enlarging the subspace, i.e., by including more of the stabilization eigenvectors, the CRISES results approach more and more closely the exact, full CR results.

It must be emphasized here that neither the initial choice of subspace nor its subsequent enlarging should be made in an arbitrary fashion. As an illustration, a 7–18 CRISES calculation was performed. The resulting θ trajectory was so featureless that a resonance kink could not be located. Yet, the dimension of the subspace, 12, is equal to that arising in a 12–23 CRISES calculation which yielded a very respectable result (see Table VI). Moreover, a 9–21 CRISES calculation gave as resonance parameters $E = 4.7679$ and $\Gamma = 0.001994$, which are clearly inferior to those of a 12–24 CRISES calculation (see Table VI), although the subspace dimensionality is the same, 13, in both calculations. What the 7–18 and 9–21 calculations have in common is that the selection of the subspaces was made ignoring the list of $|C(\eta)_{\mathrm{R},n}|$'s in Table V. Consequently, several important states, relatively strongly coupled to the resonance state (measured by the magnitude of their $|C(\eta)_{\mathrm{R},n}|$'s) were left out. An additional important point emerges from these two examples (and numerous other CRISES calculations we have performed): the energy difference $|E_\mathrm{R} - E_n|$ occurring in the denominator of $|C(\eta)_{\mathrm{R},n}|$ plays a secondary role in determining the importance of a continuum state, Φ_n, in the present context. Evidently, states which have to be included and which were missing from both of the above (7–18, 9–21) CRISES calculations (for example, states 19–24, in the 7–18 CRISES calculation, or states 22–24 in the 9–21 calculation) lie 7–19 au above the resonance state (see Table IV). Inclusion of states 7–11, which are very close in energy to the resonance state (see Table IV) helped little. In summary, the selection of states to be included in the subspace has to be systematic, the criterion being the strength of their coupling to the resonance state, measured by the magnitude of $|C(\eta)_{\mathrm{R},n}|$.

The resonance energies apparently converge faster than the widths as the subspace quality is improved. This should not be too surprising; the stabilization eigenvector subspace includes the resonance state which, as we know, has an energy very close to the exact resonance energy. Consequently, an essentially exact position of the resonance can be obtained by using subspaces of considerably smaller dimensions; a 12–24 CRISES calculation yields the exact resonance energy, but the width is still ~13% off.

We have observed, in numerous calculations, that the CRISES θ trajectories follow closely the full CR trajectories. A representative example of this is shown in Figure

TABLE VI: Resonance Energy and Width (in au) for the Model Two-Channel Problem

	CRISES[b] calculation		CRISES[b] + eq 24[c]		eq 24[d]	
states[a]	E_r	Γ	E_r	Γ	E_r	Γ
12–21	4.7679	0.001957	4.7681	0.001900	4.7680	0.001900
12–23	4.7681	0.001724	4.7681	0.001470	4.7681	0.001583
12–24	4.7682	0.001598	*e*	*e*	4.7680	0.001133
11–24	4.7682	0.001545	4.7682	0.001453	4.7682	0.001472
9–26	4.7682	0.001441	4.7682	0.001402	4.7682	0.001393
7–28	4.7682	0.001423	4.7682	0.001416	4.7682	0.001416

Resonance parameters determined by full complex coordinate rotation calculation:[29,33] $E_\mathrm{r} = 4.7682$; $\Gamma = 0.001420$

[a] Eigenvectors included in the subspace. [b] Coordinate rotation in stabilization eigenvector subspace. [c] CRISES + second-order correction (eq 24) at *every point* of the θ trajectory. [d] Second-order correction (eq 24) is added *only* to the resonance "kink" located on a CRISES θ trajectory. [e] The location of the resonance could not be determined from the perturbation trajectory.

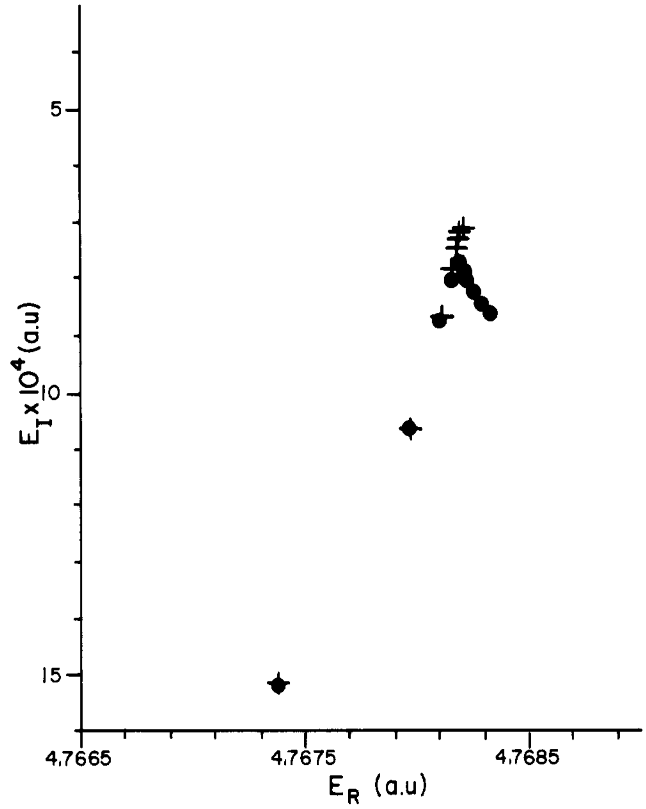

Figure 5. The θ trajectories of the resonance eigenvalue of the model two-open-channel potential problem: (+) full coordinate rotation θ trajectory; (●) 11–24 CRISES θ trajectory.

5. The CR and CRISES θ trajectories differ markedly in one aspect; while the resonance located by the former is almost perfectly stable over a wide range of angles θ, such is not the case for the CRISES trajectory (see Figure 5).

The results in Table VI demonstrate, for this model two-open-channel problem, the viability of the CRISES approach. They show that CR calculations can be performed, with very acceptable results, in a subspace which includes but a fraction of the total number of stabilization eigenvectors (12–14 out of the total of 36 eigenvectors, in our case). This drastically reduces the computational effort associated with repeated diagonalizations of the complex symmetric matrices.

In addition to the results presented above for the Noro–Taylor model problem we performed a few preliminary CRISES calculations on one of the atom–diatom model systems treated previously in section III. The results were also very encouraging, being essentially identical with those obtained in a full CR calculation.

Can the CRISES results be further improved by taking the rest of the stabilization spectrum into account via perturbation theory? Winkler and Yaris[31] concluded, for the case of the ^{1}S He resonance, that, while the second-order perturbation correction did not change the result remarkedly, it affected the backbending ("kinking") of the θ trajectory (see Figure 1 of ref 31). Moiseyev and Certain[34] applied high-order nondegenerate and almost-degenerate perturbation theory to CR calculations of ^{1}S He resonances. Their concluding opinion was that the perturbation approach was not likely to have general utility, mainly because the radii of convergence of the series were often found to be too small.

The second-order perturbation theory estimate of the effect of the neglected stabilization eigenvectors on the resonance energy and width obtained by our subspace diagonalization scheme is given by

$$E_R^{(2)}(\eta) = \sum_{n \notin S} C(\eta)_{R,n} \tag{24}$$

The notation is that of eq 23. The $n \notin S$ symbol means that the states belonging to the "important" subspace are to be omitted from the summation. Clearly, we have divided the stabilization eigenvectors (states) into two classes. In the first class are those continuum states Φ_n which, judging by the magnitude of their $|C(\eta)_{R,n}|$'s, interact strongly with the resonance state. They, together with the resonance state, form a basis in which the CRISES calculations are performed. The continuum states in the second class, considered less important because of their smaller $|C(\eta)_{R,n}|$'s and therefore left out of the complex diagonalization subspace, are summed over in the second-order perturbation correction in eq 24.

Such perturbative correction of CRISES results can be accomplished in two ways. In one, the correction $E_R^{(2)}(\eta)$ is added to the (complex) eigenvalue of the resonance state, as calculated via CRISES, at *every point* of the θ trajectory. If this scheme were to work, the corrected or perturbed θ trajectory should reveal a resonance kink thereby yielding the energy and width.

The second alternative is to locate the resonance ("kink") via the original CRISES θ trajectory. The CRISES resonance energy and width can then by corrected by adding the perturbation correction $E_R^{(2)}(\eta_0)$. Here $\eta_0 = \alpha_0 e^{i\theta_0}$ is the critical value of the scaling parameter η, as determined from the CRISES θ trajectory.

The results obtained by implementing both of these perturbation correction approaches are given in Table VI. It appears that $E_R^{(2)}(\eta)$ corrections affect the CRISES results in a rather unpredictable, ill-defined, and not always beneficial mannr. Sometimes resonance positions and widths are improved, but not significantly. In other instances the agreement with the exact results is actually worsened. In one calculation (12–24, in Table VI) the resonance (kink) could not be located at all with this perturbation trajectory. In our opinion, making the $E_R^{(2)}(\eta)$ correction is not advisable; it is certainly not worth the effort.

V. Concluding Remarks

We have shown that the stabilization method is capable of yielding accurate energies of one- and two-open-channel resonances in triatomic systems. We have also shown that the widths of rotational Feshbach resonances of atom–diatom systems can be calculated, with good accuracy, using two eigenvectors obtained via the stabilization method and Miller's "golden rule" formula. It was especially satisfying to demonstrate that the specific "golden rule" expression used here, until now tested only on electronic autoionization lifetimes of atoms and molecules, can be successfully applied to heavy particle predissociation phenomena. The present procedure poses no severe computational problems since it consists essentially of repeated diagonalizations of (real) Hamiltonian matrices for various values of the scaling parameter α. It appears to be particularly suitable for narrow resonances since, in these cases, the resonance eigenvalues are very "stable", thereby making the extrapolation arising in the implementation of the "golden rule" expression more precise and presumably accurate. Thus, the present procedure seems to complement the range of efficiency of the more common (e.g., phase shift analysis) scattering calculations where it is often difficult to locate narrow resonances since the jump in phase occurs over a very small energy range.

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It is likely that the stabilization and golden rule procedure can be readily applied to vibrational Feshbach resonances as well. Eastes and Marcus have successfully used the stabilization method to locate such resonances in atom-diatom oscillator colinear collisions,[35] although they made no attempt to evaluate the resonance widths. Location of resonances by performing scattering calculations proved in the case (narrow resonances) treated in ref 35 to be very difficult. This again supports our belief that the present L^2 method will be useful in supplementing conventional scattering techniques.

Considering our results on the model two-open-channel problem as well as work of Winkler and Yaris[31] it seems that the stabilization procedure provides a good starting point for a more efficient, less time-consuming version of the coordinate rotation technique. Subspaces of stabilization eigenvectors, selected via second-order perturbation theory, allow for significant reduction in the dimensionality of the complex symmetric matrices to be diagonalized in the course of computing θ trajectories. This saving may be particularly important for many-open-channel problems where the matrix dimensions can quickly become prohibitively large. The results obtained via this scheme compare favorably with full coordinate rotation results. Accounting for the neglected part the stabilization eigenvector spectrum by second-order perturbation theory does not seem worthwhile in light of our results.

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Stochastic Calculation of Interaction Energies

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A Monte Carlo method by which the properties of a collection of interacting nuclei and electrons might be accurately calculated is briefly outlined. This method allows quantitative determination of the pairwise intermolecular potential and potential surfaces but eliminates the use of these constructs for dense systems. Preliminary results on the electron gas, hydrogen solid, and the molecules He_2, LiH, Li_2, and H_2O are at least as accurate as the best previous work.

Introduction

Great progress has been made in recent years in quantitatively calculating the equilibrium properties of bulk matter just from knowledge of the interactions of the constituent atoms or molecules, provided these behave classically. This has been made possible through the Monte Carlo method, carried out on computers.[1] This method overcomes the mathematical difficulty of evaluating high-dimensional integrals, such as the partition function, by sampling configurations of the system, chosen according to their Boltzmann weight. The desired integral averages over these configurations are readily carried out for any property. The accuracy of the result for a given number of particles is only limited by the number of configurational averages that are practical to perform.

Very complex systems, such as long hydrocarbons and polymer fluids, have been simulated in this way, using simplified model intermolecular potentials. Although in these complex systems it is very time consuming to move from one configuration to another, the true limitation in the quantitative comparison to experiments rests in the need for accurate knowledge of the intermolecular potential. This is true even for the simplest known liquids-namely, those of the rare gases. The intermolecular potential, which is the only input required in these calculations, is usually derived empirically from low-density data. Such data as transport coefficients and second virial coefficients are most commonly used, because this information can be readily inverted to yield an intermolecular pair potential. Further, very useful information about the pair potential can be derived from spectroscopic and molecular beam experiments. The best pair potential deduced from all these experiments, however, fails to quantitatively predict the dense fluid properties even for argon.[2] This is because the total potential is not accurately represented by the sum of pairwise potentials thus derived. Very little is known about higher-order corrections to the pairwise additive potential. Somewhat surprisingly, however, when the asymptotic triplet correction is added, in the case of the rare gases, most fluid properties are nearly quantitatively predicted.

Nevertheless, this is not a satisfactory situation from the statistical-mechanical point of view. First of all, in the process of obtaining the intermolecular potential, the statistical mechanical expressions valid at low density are utilized. This logic deprives us of any hope of calculating low-density properties from first principles. Secondly, the inversion process by which the intermolecular potential is derived is not unique. Furthermore, the interaction of

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