Resonance state energies and lifetimes via analytic continuation of stabilization graphs

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In this paper, we determine the lifetimes of three chemical reaction resonance states by analytically continuing real-valued stabilization graphs into the complex-energy plane. Extending the method developed by Simons in 1981, we estimate the widths of the resonances by fitting the stabilization graphs to a two-branched quadratic equation whose coefficients are polynomials in the real-scaling parameter α. We also study what criteria affect the quality of the resonance-state lifetime and develop a systematic procedure that could be followed to determine such lifetimes.

I. INTRODUCTION

Using the stabilization method[1] one can estimate the energies of long-lived metastable states of a wide variety of species. To obtain lifetimes for these metastable states, there exist a number of techniques[2–4] (e.g., "Golden Rule" methods, Siegert methods, and complex-coordinate-rotation method) most of which require knowledge of the stabilized-state eigenvector. Because of the computational difficulty of determining these eigenvectors, simpler techniques which use only eigenvalue information have received considerable attention.[5–10]

In 1981, Simons[5] demonstrated that one could *estimate* the desired lifetime directly from the stabilization graph by making a connection, via analytic continuation, with the complex-coordinate-rotation (CCR) method in which the negative imaginary part of the energy is associated with the lifetime by the following equation:

$$E = E_R - i\frac{\Gamma}{2}, \tag{1}$$

where Γ is the width of the metastable state from which the lifetime can be determined. He showed how to estimate, "on the back of an envelope," the lifetime for cases in which the eigenvalues undergoing an avoided crossing vary almost linearly as functions of the real-scaling parameter α in the neighborhood of the avoided crossing. Since that time, numerous articles[6–10] describing alternative methods for determining lifetimes of resonance states by analytically continuing real-valued stabilization graphs into the complex-energy plane have appeared:

(1) Thompson and Truhlar[6] calculated resonance positions and widths for $H + H_2$ and $H + HF$ by fitting to a single-valued polynomial in α the energy of *one branch* of the avoided crossing. The resulting lifetimes were found to lie within a factor of 2 or 3 of those obtained by highly accurate methods.

(2) Thirumalai *et al.*[7] tried to use single-valued rational functions to fit the resonant eigenvalue. They were able to achieve trends rather than quantitative predictions of the lifetimes for $H + H_2$, $H + HF$, and $F + H_2(D_2,DH)$.

(3) McCurdy and McNutt[8] realized that problems in continuing the energy *eigenvalues* to complex values were caused by branch points near the real axis in the complex-energy plane. To overcome this problem, they analytically continued the *coefficients* of a multivalued energy-fitting polynomial rather than the energy function itself. Their results reproduce the energies and widths of a one-particle model potential to two or three significant figures if they utilized, as input data, the energy at quite a few values of α.

(4) Issacson and Truhlar[9] set forth a method which avoids the problem of branch points by continuing the scaling factor α into the complex plane, yet still uses only the resonant eigenvalue. Using the same number of data points as parameters, they fit the resonant eigenvalue to the roots of a quadratic equation $E^2 + P_1E + P_0 = 0$ where P_0 and P_1 are polynomials in α and E is the energy function. Their best results are within approximately 10% of the accurate lifetimes for a model involving s-wave scattering of an electron from a central potential.

(5) Löwdin[10] rederived Simons' formula without making the assumption of local linearity of the stabilization energy curve. His derivation was also made in terms of a quadratic equation in E whose coefficients are polynomials in α.

In light of the numerous developments which have been made since the 1981 paper, we decided to further examine and extend our own technique in order to better determine the sensitivity of our method. In the spirit of our earlier work, as well as the works of Issacson and Truhlar[9] and Löwdin,[10] we fit the energies of the stabilization plots using a quadratic equation for the energy function with the coefficients which are polynomials in the real-scaling parameter α. After determining the optimal polynomial coefficients, the value of α is then allowed to become complex to achieve the continuation of our energy expression into the complex plane. As in the complex-coordinate-rotation method, the (complex) value of E at which variations in E with respect to variations in (complex) α vanish is identified as the energy to be used in Eq. (1).

II. METHOD

A. Determining the polynomial coefficients

A typical stabilization graph for a one-open-channel system is shown in Fig. 1. The two eigenvalues corresponding to the avoided crossing can be thought of as arising from the interaction of two zeroth-order states through a two-

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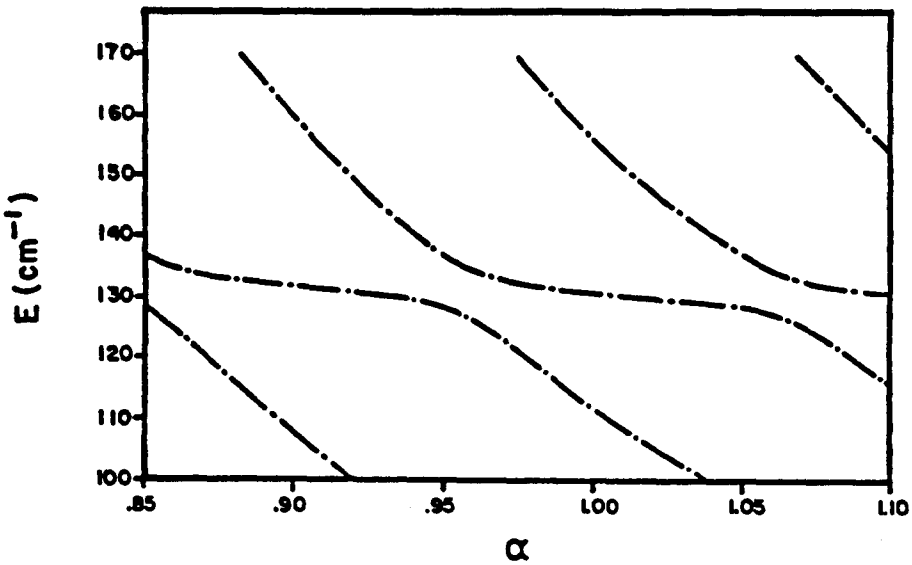

FIG. 1. Typical stabilization graph for a one-open-channel system.

dimensional secular equation of the form:

$$\begin{vmatrix} H_{11}(\alpha) - E & V(\alpha) \\ V(\alpha) & H_{22}(\alpha) - E \end{vmatrix} = 0\,, \tag{2}$$

where $H_{11}(\alpha)$ is the energy of the slowly varying resonance root, $H_{22}(\alpha)$ is the energy of the nonresonance continuum root, and $V(\alpha)$ represents the interaction between the two roots. We prefer to write this as a secular equation because of the intuitive picture it gives.

The eigenvalues from Eq. (2) are given by

$$E_{\pm} = 1/2(H_{11}(\alpha) + H_{22}(\alpha) \pm \{[H_{11}(\alpha) - H_{22}(\alpha)]^2 + 4V(\alpha)^2\}^{1/2}) \tag{3a}$$

which is of the form

$$E_{\pm} = 1/2\{H_{+}(\alpha) \pm [H_{-}(\alpha)^2 + 4V(\alpha)^2]^{1/2}\}\,, \tag{3b}$$

where $H_{+}(\alpha)$ and $H_{-}(\alpha)$ are the sum and difference of H_{11} and H_{22}, respectively. The functions $H_{+}(\alpha)$,$H_{-}(\alpha)$, and $V(\alpha)$ are expressed as polynomials in the real parameter α whose coefficients are determined by the *least-squares fitting* of the two eigenvalues in the stabilization graph to Eq. (3b). The least-squares function F minimized to achieve this fit is

$$F = \sum_i (1/2\{H_{+}(\alpha_i) \pm [H_{-}(\alpha_i)^2 + 4V(\alpha_i)^2]^{1/2}\} - E_i)^2\,, \tag{4}$$

where the sum is over the "data points" E_i. The energy E_i is the value of either *one* of the stabilization energies obtained at the real value of the scale parameter denoted α_i.[11]

B. Determining the lifetime

The lifetimes are determined by first analytically continuing the polynomials [$H_{+}(\alpha)$,$H_{-}(\alpha)$, and $V(\alpha)$] into the complex α plane. Then we seek values of α for which $(dE/d\alpha) = 0$, since one of the two eigenvalues of Eq. (3b) is expected[1] to display, in the region of the avoided crossing between $H_{11}(\alpha)$ and $H_{22}(\alpha)$, the kind of stable behavior found in coordinate-rotation (CR) theory. The continuation into the complex plane is accomplished by first examining the conditions under which the two roots of Eq. (3b) become degenerate. This occurs at a complex value of α (denoted $\bar{\alpha}$), where

$$H_{-}(\alpha)^2 + 4V(\alpha)^2 + 0\,. \tag{5}$$

To find $\bar{\alpha}$ we solve Eq. (5) using the Newton–Raphson method. Then, expanding the eigenvalues in Eq. (3b) around $\bar{\alpha}$, we generate a set of equations for the real and imaginary parts of the energy as functions of $\alpha - \bar{\alpha}$. By looking for a stable point in the resulting energy expression, $(\partial E/\partial\alpha) = 0$ in the vicinity of $\bar{\alpha}$, we determine [Eq. (1)] the width from the imaginary part of the complex energy at this stable point.

C. Systems studied

We studied two timely and important chemical systems using the method described above: the H + HF[12,13] and H + H_2[14] chemical reaction resonances. Garrett *et al.*[15] have studied the resonances of the collinear reaction H + HF by coupled-channel-scattering calculations. The H + H_2 system was studied by Schatz and Kupperman.[16] Thompson and Truhlar[6] used the collinear reactions of both of these systems in their analytic-continuation study, as did Thirumalai *et al.*[7] Although the potential energy surfaces used may be viewed as model potentials, resonances on the F + H_2 surface and its isotopic analogs may have been seen experimentally.[17]

We examined the 15.35 and 17.81 kcal/mol resonances of the collinear H + HF system and the 20.1 kcal/mol resonance of the collinear H + H_2 system. We selected these cases because the stabilization graphs for H + HF were found to be quite nonlinear in α as, to a lesser degree, were those of the H + H_2 system. This allowed us to see how the present extension of our earlier method works with two quite different types of α dependence. Also, since there have been

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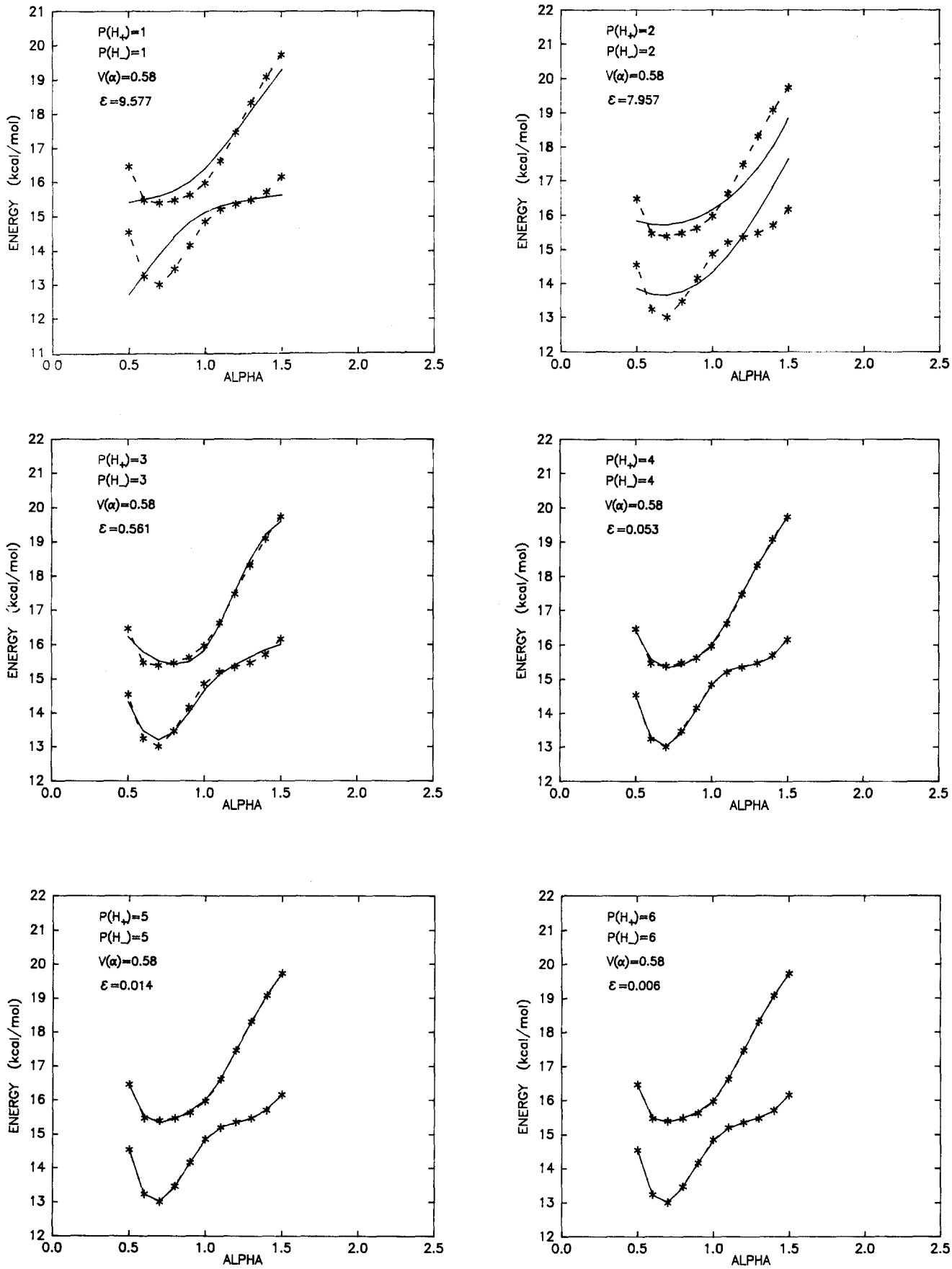

FIG. 2. Fits of the stabilization graph for the resonance at 15.71 kcal/mol in the H + HF system. The interaction polynomial $V(\alpha)$ is not optimized in the least-squares minimization in these fits. The dashed line is the data and the solid line is the least-squares fit to the data. The data points used to determine the least-squares fit are denoted by *. $P(H)$ is the order of the $H(\alpha)$ polynomial. ϵ is the least-squares error.

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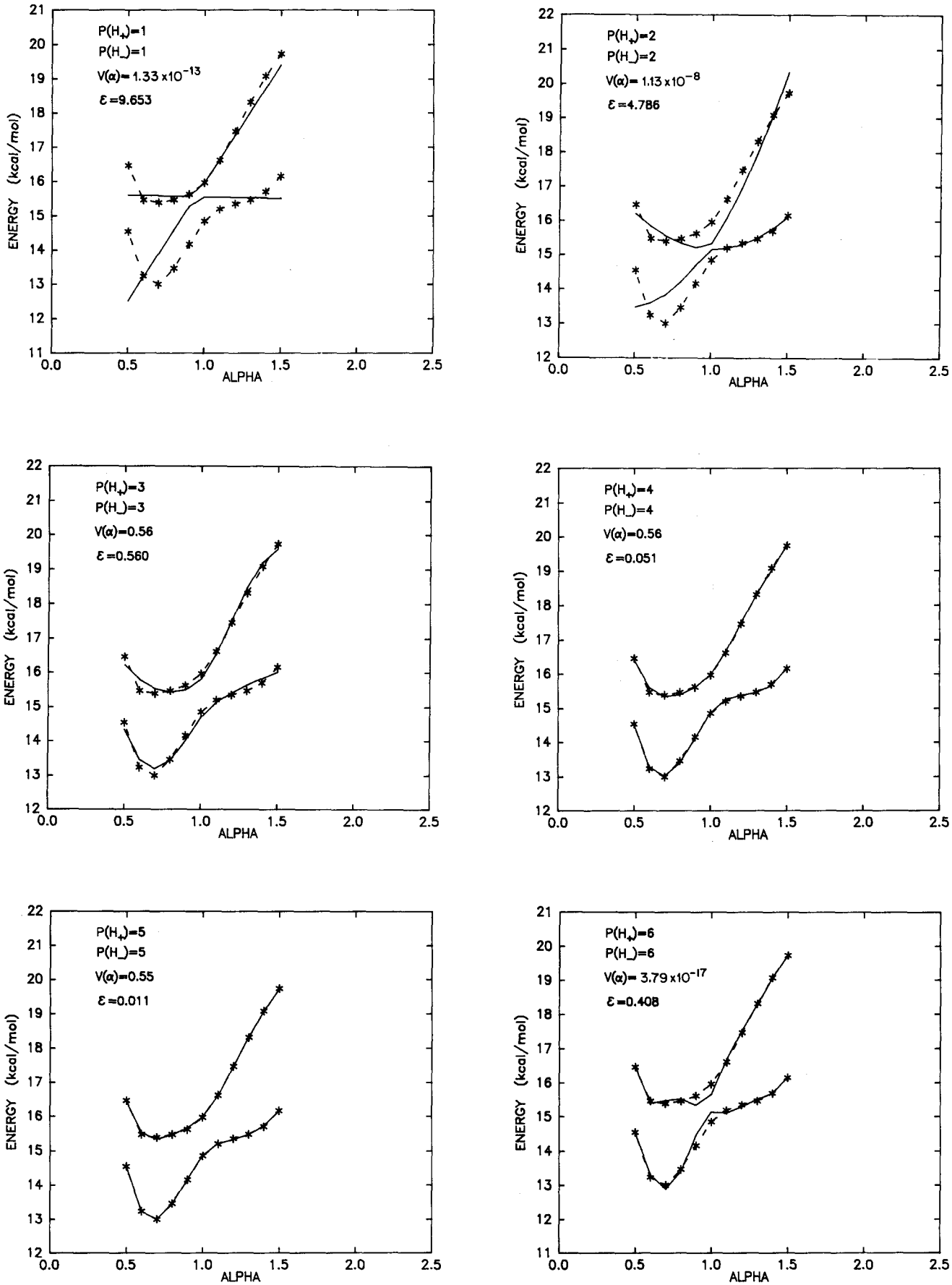

FIG. 3. Fits of the stabilization graph for the resonance at 15.71 kcal/mol in the H + HF system. The interaction polynomial $V(\alpha)$ is optimized in these fits. The dashed line is the data and the solid line is the least-squares fit to the data. The data points used to determine the least-squares fit are denoted by *. $P(H)$ is the order of the $H(\alpha)$ polynomial. ϵ is the least-squares error.

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coupled-channel-scattering calculations on the above resonances,[15,16] we can compare our results to accurate quantal results.

Most of the data used in this study were extracted from the stabilization graphs of Thompson *et al.*[6]; we estimate that our reading of these graphs limits the precision of our results to two digits which we feel is adequate.

III. RESULTS

A. H + HF (resonance at 15.35 kcal/mol)

To fit the stabilization graph of Ref. 6 for the resonance at 15.35 kcal/mol of H + HF (Figs. 2 and 3) we used a greater number of data points then polynomial coefficients; in contrast, Issacson and Truhlar[9] used the same number of data points as unknown coefficients. As a result, we use a least-squares method to fit our data whereas in Ref. 9 the data uniquely determine the coefficients. In carrying out our least-squares-fitting procedure, we found it necessary to use data from both branches to achieve a reasonable fit to the stabilization graph.[18]

We found it important to determine the optimal orders to use for the polynomials $H_+(\alpha)$ and $H_-(\alpha)$ given a specific set of energy "data." In our first attempts at developing a systematic procedure, we approximated the interaction polynomial $V(\alpha)$ by a zeroth-order polynomial in α with a value *fixed* at one-half of the minimum separation between the two branches of the stabilization energies. This choice was found to be reasonable in our earlier studies[5] and was further supported by subsequent study (see later). We then increased the order of the polynomials used to describe $H_+(\alpha)$ and $H_-(\alpha)$ and minimized the least-squares function F [Eq. (4)] with respect to the coefficients in the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials. The results obtained via these fits are shown in Fig. 2. We observed that as the order of the $H_\pm$ polynomials increased, the fit and the least-squares error improved monotonically until the fit was no longer a least-squares fit at which point the routine became slightly unstable. Clearly, this process does not determine the optimal order for the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials, although inspection of Fig. 2 convinces one that orders of at least four are necessary in this case. In our next attempts, the above process was repeated, this time including an optimization of the value of the interaction term V. As shown in Fig. 3, as the orders of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials were increased, the fits became more accurate until the polynomials reached an order of 5, after which the quality of the fits actually deteriorated because the least-squares-fitting function started to converge to a saddle point. This is caused by having more parameters in $H_+(\alpha)$, $H_-(\alpha)$, and $V(\alpha)$ than could reasonably fit the data utilized. We also noted that the optimal value of the interaction term V became approximately equal to zero when the order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials were greater than 5. The best fits (as measured by the least-squares criterion) were obtained (see Fig. 3) when the value of the interaction term V was optimized and was found to be approximately one-half of the minimum separation of the two branches, thereby supporting our earlier observations.

Having described our criteria for choosing the order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials, let us now examine the sensitivity of our estimated widths to taking data from various parts of the stabilization curves. Fits A, B, and E in Table I under fitting scheme I were generated by using data points chosen both near to and farther away from the avoided crossing. The resulting widths are within a factor of 3 of the accurate value. Fits C, D, and F were obtained using only data points from near the avoided crossing. The resulting widths are only within a factor of 1.7 of the accurate value. As seen previously,[6] the calculated widths are dependent on the data points used. We have found that the widths become less accurate as points far from the avoided crossing are included, even if the majority of the points are in the vicinity of the crossing.

TABLE I. H + HF system: Resonance at 15.35 kcal/mol. Accurate (Ref. 15): $\Gamma = 0.48$ kcal/mol, $E_R = 15.35$ kcal/mol.

Fit	Order of polynomial	Sampling area	Γ (kcal/mol)	E_R (kcal/mol)	Least-squares error
Fitting scheme I (see the text for notation)					
A	3	a	1.4	15.3	0.560
B	4	a	1.3	15.5	0.051
C	4	b(11)	0.74	15.3	$<1.0\times10^{-10}$
D	4	b(11)	0.81	15.2	$<1.0\times10^{-10}$
E	5	a	1.1	15.5	0.011
F	5	b(13)	0.62	15.7	$<1.0\times10^{-10}$
Fitting scheme II (see the text)					
C1	3	b(8)	0.54	15.3	0.001
C2	3	b(11)	0.61	15.3	0.000
F1	4	b(11)	0.49	15.6	5.1×10^{-6}
F2	4	b(12)	0.41	15.7	1.5×10^{-5}
F3	4	b(10)	0.35	15.6	$<1.0\times10^{-10}$

[a] All the data points were used (total number of points used was 22).

[b] Only data points near the avoided crossing were used; the number of points used is in parentheses. The fits using the same order of polynomial and the same number of points differ by the positions of the points used. In fitting scheme II, the points used are in the range 0.75–1.0 α units.

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In an attempt to further improve the quality of our calculated width, we used the optimized polynomial coefficients of fits C and F to generate, via Eq. (3b), additional interpolated data points local to the avoided crossing for use in additional least-squares fitting. We felt that by utilizing more data points near the avoided crossing we should obtain a better width. The obvious way for us to accumulate more data points is to generate, via Eq. (3b), our own *interpolation* of the data. The original data were 0.1 α units apart; the new interpolated data are 0.05 α units apart. We recalculated new widths using these data points by keeping V approximately one-half of the minimum separation of the two branches and by *lowering* the order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials by one. For example, since fit C involves quartic polynomials for $H_\pm$, we used cubic polynomials to fit the new data set (original plus interpolated) generated by using the coefficients of fit C. Because we generated the new data from the calculated coefficients of the polynomials which fit the original data, we could not use the same order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials when fitting the new data. Therefore we lowered the order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials to help smooth out (i.e., interpolate) the curve.

As shown in Table I under fitting scheme II, the results obtained using the interpolated data generated as described above (fits C1, C2, F1–F3) give widths even closer to the quantal width. The mean value of the widths calculated using a cubic order for the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials (fits C1 and C2) is within 20% of the accurate lifetime; the mean value of the lifetimes calculated using a quartic order for the polynomials (fits F1–F3) is within 13% of the accurate width. We repeated the above process with data points that were even closer together (0.03 α units apart) and obtained results similar to those obtained using data points 0.05 α units apart. Therefore, we feel that any of fits F1–F3 represents our best efforts.

B. H + HF (resonance at 17.81 kcal/mol) and H + H_2 (resonance at 20.1 kcal/mol)

We repeated the same technique as outlined above for the resonance at 17.81 kcal/mol in the H + HF system (Fig. 4) and for the resonance at 20.1 kcal/mol in the H + H_2 system (Fig. 5). The calculated widths for the resonance at 17.81 kcal/mol in H + HF are listed in Table II. By using the same process as outlined above, we determined the optimal order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials to be cubic. To determine which fit to use in generating our interpolated data points local to the avoided crossing, we drew upon our experience with CR since the least-squares error for most of the fits are approximately the same. In CR we have found that the better the calculation is the narrower the calculated width becomes. Hence, we used the coefficients from fit B to interpolate the data since this fit gave us the narrowest width. The mean value of the widths calculated from fitting these interpolated data points (fits B1–B4) is within 15% of the accurate width. These results are listed in Table II under fitting scheme II. Excluding the one case (fit B2) with unusually large least-squares error, the fits are within 6% of the correct lifetime.

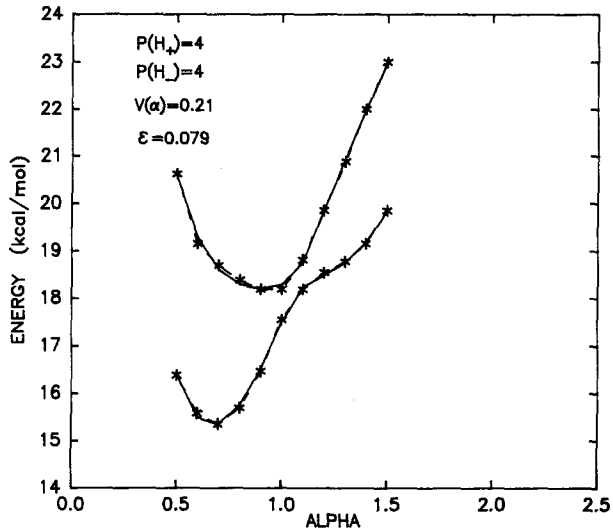

FIG. 4. A fit of the stabilization graph for the resonance at 17.81 kcal/mol in the H + HF system. The interaction polynomial $V(\alpha)$ is optimized in this fit. The dashed line is the data and the solid line is the least-squares fit to the data. The data points used to determine the least-squares fit are denoted by *. $P(H)$ is the order of the $H(\alpha)$ polynomial. ϵ is the least-squares error.

The calculated widths for the resonance at 20.1 kcal/mol in H + H_2 are listed in Table III. The data used in calculating the widths for this resonance were taken from stabilization calculations performed by Thompson and Truhlar[19] instead of from the stabilization graphs of Ref. 6. Initially we attempted to obtain data from the stabilization graph (as we did with the resonances in H + HF), but we could not achieve a reasonable approximation to the accurate data because the graph appears to be quite linear in α (Fig. 5) and the resolution available to us by sight limited the accuracy of our data. Using the same procedure as before, the optimal

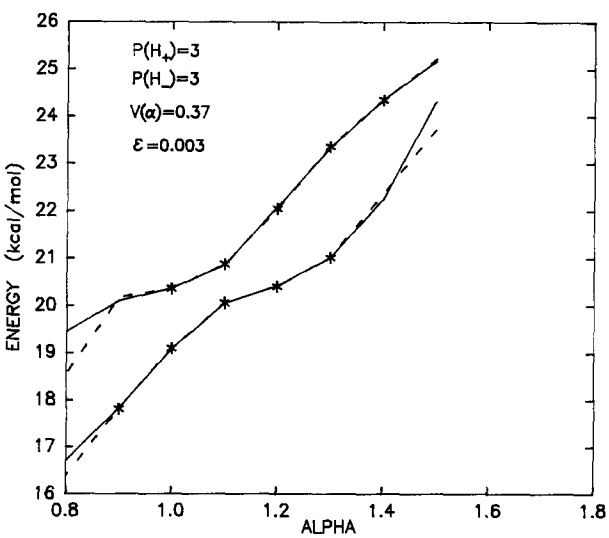

FIG. 5. A fit of the stabilization graph for the resonance at 20.1 kcal/mol in the H + H_2 system. The interaction polynomial $V(\alpha)$ is optimized in this fit. The dashed line is the data and the solid line is the least-squares fit to the data. The data points used to determine the least-squares fit are denoted by *. $P(H)$ is the order of the $H(\alpha)$ polynomial. ϵ is the least-squares error.

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TABLE II. H + HF system: resonance at 17.81 kcal/mol. Accurate (Ref. 15): $\Gamma = 0.26$ kcal/mol, $E_R = 17.81$ kcal/mol.

Fit	Order of polynomial	Sampling area	Γ (kcal/mol)	E_R (kcal/mol)	Least-squares error
Fitting scheme I (see the text)					
A	3	a	0.59	18.2	0.271
B	3	b(9)	0.31	18.3	$<1.0\times10^{-10}$
C	3	b(9)	0.47	18.2	$<1.0\times10^{-10}$
D	3	b(9)	0.68	18.1	$<1.0\times10^{-10}$
E	3	b(9)	0.50	18.1	$<1.0\times10^{-10}$
F	4	a	0.52	18.3	0.079
G	4	b(11)	0.43	18.2	$<1.0\times10^{-10}$
H	4	b(11)	0.73	17.7	1.2×10^{-5}
Fitting scheme II (see the text)					
B1	2	b(6)	0.26	18.3	$<1.0\times10^{-10}$
B2	2	b(8)	0.48	17.8	0.021
B3	2	b(7)	0.24	18.2	4.4×10^{-5}
B4	2	b(8)	0.23	18.3	9.8×10^{-5}

[a] All the data points were used (total number of points used was 22).
[b] Only data points near the avoided crossing were used; the number of points used is in parentheses. The fits using the same order of polynomial and the same number of points differ by the position of the points used. In fitting scheme II, the points used are in the range 0.95–1.10 α units.

degree of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials was determined to be 3. From the coefficients of our best least-squares fit (fit D) we generated interpolated data points near the avoided crossing. The mean value of the width calculated by fitting these points (fits D1–D5) is within 6% of the accurate width.

IV. CONCLUSIONS

As we stated previously, we wanted to see what criteria affected the quality of the estimate of the resonant state lifetime calculated using the method of Ref. 5. We also wanted to determine a systematic procedure that one could follow to get the estimate.

We fit the stabilization graphs with a quadratic energy equation whose coefficients are polynomials in the real-scaling parameter α by using a nonlinear least-squares method. We then analytically continued the polynomials in α into the complex plane and determined the lifetime from the imaginary part of the complex energy at a stable point.

The procedure we used to find an estimate of the lifetime can be outlined as follows. First, we determine an optimal order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials by allowing the interaction polynomial $V(\alpha)$ to be varied along with the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials. We use the orders of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials where the least-squares error is good and the value of the interaction term V is deter-

TABLE III. H + H_2 system. Accurate (Ref. 16): $\Gamma = 0.51$ kcal/mol, $E_R = 20.1$ kcal/mol.

Fit	Order of polynomial	Sampling area	Γ (kcal/mol)	E_R (kcal/mol)	Least-squares error
Fitting scheme I (see the text)					
A	2	a	0.97	20.3	0.146
B	2	b(10)	0.79	20.4	0.020
C	3	a	0.92	20.3	0.065
D	3	b(10)	0.78	20.4	0.003
Fitting scheme II (see the text)					
B1	1	b(6)	0.49	20.2	0.011
B2	1	b(6)	0.41	20.0	0.003
B3	1	b(6)	0.51	20.5	0.004
B4	1	b(6)	0.44	20.3	0.004
D1	2	b(8)	0.55	20.3	0.033
D2	2	b(8)	0.51	20.1	0.044
D3	2	b(8)	0.70	20.2	0.002
D4	2	b(10)	0.33	20.2	0.002
D5	2	b(10)	0.29	20.3	0.003

[a] All the data points were used (total number of points used was 16).
[b] Only data points near the avoided crossing were used; the number of points used is in parentheses. The fits using the same order of polynomial and the same number of points differ by the position of the points used. In fitting scheme II, the points used are in the range 0.80–1.15 α units.

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mined to be approximately one-half of the minimum separation of the two branches. We then calculate the widths using only data points near the avoided crossing. Finally, to achieve a better estimate of the lifetime, we generate new data ponts more local to the avoided crossing by using the specific fit of the actual stabilization data which yields a good least-squares residual and which gives the narrowest width. We fit these new data points by lowering the order of the $H_+(\alpha)$ and $H_-(\alpha)$ polynomials by one power of α. This lowering of the order of the polynomials is done to smooth out the curve. Since the resulting lifetime is dependent on the choice of data points used for the fitting, we pick several different sets of points to fit and take the mean value of the resulting lifetimes, assuming they are all of good least-squares fits. We find that the mean value of the lifetimes is usually within 6%–20% of the accurate quantal lifetimes.

We studied two systems, H + HF and H + H_2, using the above procedure. The mean values of the calculated lifetimes for the resonances at 15.35 and 18.71 kcal/mol in the H + HF system were within 13% and 6% of the accurate lifetime, respectively. For the resonance at 20.1 kcal/mol in the H + H_2 system, the mean value of the calculated lifetimes was within 6% of the accurate lifetime.

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