Quantum reactive scattering in three dimensions using hyperspherical (APH) coordinates. VI. Analytic basis method for surface functions

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(Received 17 November 1992; accepted 29 December 1992)

We continue development of the theory of reactive (rearrangement) scattering using adiabatically adjusting principal axes hyperspherical (APH) coordinates. The surface functions, functions of the APH hyperangles covering the surface of the internal coordinate sphere, are expanded in analytic basis functions centered in each of the arrangement channels. The rotational functions are associated Legendre polynomials, and the vibrational functions are harmonic functions of an "anharmonic" variable which covers an infinite range, allows accurate Gauss-Hermite quadrature, and includes effects of anharmonicity. Example calculations show that these functions provide an efficient basis which can markedly decrease the computational effort required to generate accurate surface functions.

I. INTRODUCTION

Recent years have seen very rapid development of new quantum methods for treating reactive molecular collisions (rearrangement scattering) in the full three-dimensional (3D) physical space.¹ These methods, together with advances in computers, now allow accurate calculations on many reactions of real chemical interest. Rapid advances are being made both in time-dependent and timeindependent methods; however, we limit discussion here to time-independent methods. The two most popular such approaches are (1) coupled channel (CC) expansions using hyperspherical coordinates and (2) "variational" arrangement channels expansions using Jacobi coordinates, and there are several methods differing in detail within each approach. Both approaches have had remarkable successes on many systems¹ and have often leapfrogged each other in the difficulty of system they could handle. At the moment, the two most difficult systems for which complete differential or integral cross sections have been reported are the $F+H_2 \rightarrow HF+H$ reaction^{2,3} and the $He+H_2^+ \rightarrow HeH^++H$ reaction,⁴ and, on both, the most extensive results over the widest energy range have been obtained by the hyperspherical method of Launay and co-workers^{2,4} which differs only in minor ways from the method we have presented in the papers in this series.⁵⁻⁹ In the present paper we show how to further improve the efficiency of these hyperspherical methods.

In hyperspherical coordinate formulations of reactive scattering, the total wave function is expanded in Wigner rotation functions of three Euler angles describing the spatial orientation of the plane formed by the three particles and basis functions of two internal hyperspherical angles, and then the dependence on the hyperradius, ρ , is determined by propagating the set of coupled channel (CC) differential equations from small ρ , where the solutions must be regular, to large ρ where they can be projected onto the arrangement channels to determine the scattering matrix. The various hyperspherical methods differ mostly in which of the many sets of hyperangles are used and how the basis functions are chosen. Most of those methods which use Delves-type^{10,11} hyperspherical coordinates expand the wave function simultaneously in three sets of hyperangles, one set centered in each arrangement channel. The basis functions in each arrangement usually consist of products of diatomic rotational functions of the internal rotational angle Θ_{τ} between the Jacobi vectors of the τ th arrangement and numerically determined "vibrational" basis functions of some multiple of the Delves hyperangle ϑ_{τ} of that arrangement. The basis functions in one arrangement are only orthogonal to those in the other arrangements at large ρ ; at small ρ they overlap to couple the arrangements.

In the methods using those hyperspherical coordinates which treat all of the particles symmetrically,^{2,4-9,12,13} one obtains "surface functions," the basis functions of the two hyperangles which cover the surface of the internal coordinate sphere or "hypersphere," by solving a twodimensional (2D) Schrödinger equation. This equation, which is discussed in more detail later in this paper, depends parametrically on ρ and must be solved at many values of ρ . In addition, a large number of these surface functions must be obtained at each ρ , so that it is important to have an efficient method for finding them.

The first accurate 3D reactive scattering calculations using hyperspherical coordinates by both others^{11(a),13} and ourselves^{5-7,14,15} used finite element methods (FEMs) to solve the surface function equation. These FEMs work reasonably well at small ρ where the surface functions are delocalized over much of the surface of the "hypersphere." However, at large ρ , where the arrangement channels are localized in small regions of the surface, it requires very fine grids to make the FEMs give accurate surface functions. Even with algorithms which make the grid coarse in classically forbidden regions, the regions of fine grid lead to rather large square matrices (typically of order $N \sim 4000$), and the subspace iteration¹⁶ (SI) method we initially used to diagonalize those matrices proved to be computationally slower than desired. Initial attempts¹⁷ to speed up the calculations with a block Lanczos¹⁸ (BL) diagonalizer proved disappointing. However, in more recent work we¹⁹ have implemented a spectral transform Lanczos method²⁰ (STLM) which is much more encouraging. In practice, the STLM is at least an order of magnitude faster than the SI or BL methods, and it makes FEM calculations feasible for many systems, especially at small ρ . Its one drawback is that, in production work, while running calculations for a series of ρ values, the STLM algorithm occasionally fails to converge, and the program stops and must be restarted.

Before leaving this discussion of the FEM method, we note that reactive scattering problems, whose potentials are nonseparable in a way that requires subdividing regions of an initially coarse finite-element grid, are not very well conditioned for use of the FEM. The FEM is capable of much higher efficiency and accuracy in problems where the grid can smoothly change from coarse to fine.²¹

A second method which we have implemented^{8,9,22} and used²³⁻²⁵ in calculations on several reactions is the discrete variable representation²⁶ (DVR). Like the FEM, the DVR is most efficient at small ρ where the surface functions are delocalized. At large ρ , where the surface functions are highly localized but the DVR points still cover the whole space, it becomes much less efficient. However, with the sequential diagonalization-truncation technique²⁷ the final matrix which must be diagonalized is usually of order n < 1000, which is significantly smaller than encountered in the FEM, and the diagonalization can be performed directly. Thus, on most systems, it is faster than the STLM-FEM, and its eigenfunctions and eigenvalues are smoother and more accurate. The code also runs very reliably. However, in a few cases where one diatomic molecule has a much shorter bond length than another, such as the HF molecule in the Li+HF \rightarrow LiF+H reaction^{14,15,28} and the $t\mu D$ molecule (where t is a tritium nucleus and μ a negative muon) in the $t\mu + D_2 \Longrightarrow t\mu D_2^* \rightarrow t\mu D + D$ reaction¹⁹ of muon-catalyzed fusion, the DVR is more expensive than the FEM because of the need for many grid points in a small, localized region. Furthermore, in systems such as e^+ +H, the DVR does not give the proper Coulomb cusp in the wave functions.

A third method for obtaining the surface functions is the finite basis representation (FBR) of Launay and LeDourneuf^{2,4,12} who expand in simple trigonometric functions closely related to the hyperspherical harmonics that are the solutions of the problem when the total angular momentum J=0 and the potential V=0. Thus, their primitive basis functions are equivalent to the FBR on which our DVR method is based, and, like the FEM and DVR methods, this FBR is efficient at small ρ but gets inefficient at large ρ . To keep the basis size manageable at large ρ . Launay and LeDourneuf^{2,4} performed a basis contraction by a prediagonalization that produces a new basis concentrated near linear and away from the symmetric top configurations that become classically forbidden at large ρ . That enabled them to generate complete cross sections for the difficult reactions already discussed. However, we believe that this FBR is not as efficient as the DVR because, for the F+H₂ reaction with J=0, this FBR required diagonalizing matrices of order as large as² N=1460 to obtain functions of the same accuracy as those obtained with the DVR with^{8,22} N<940, and the computational costs of both methods scale as N^3 .

A fourth surface function method is that of Wolniewicz and Hinze²⁹ who construct the *J*-dependent hyperspherical harmonics and use them as a primitive basis in solving for surface functions that cover the whole 5D surface of the hypersphere. These basis functions are also best at small ρ , and a contraction is necessary to keep the size of the basis manageable at large ρ . The hyperharmonics have the advantage that they exactly handle the Eckart singularities³⁰ in the rotational part of the Hamiltonian, but they have the disadvantage that they are a large, inefficient basis for many problems, and the surface function problem must then also be solved again for every *J*. Thus, for a great many problems, this approach is much more expensive than the DVR and the FBR methods already discussed.

In this paper we present a fifth method, herein denoted the analytic basis method (ABM), for obtaining surface functions. It has some similarity to the Delves hyperspherical methods of Schatz¹⁰ and Kuppermann and coworkers¹¹ in that it uses functions centered in the arrangement channels and diatomic rotational functions of Θ_r . However, our overall formulation of the problem is kept in the symmetric adiabatically adjusting principal axes hyperspherical (APH) coordinates, and Schatz and Kuppermann use numerical vibrational functions of the Delves angles ϑ_{τ} while we use analytic, simple harmonic functions of an "anharmonic" variable, z_{τ} , z_{τ} is a trigonometric function of ϑ_{τ} which covers an infinite range, allows accurate Gauss-Hermite quadrature, and allows one to include effects of anharmonicity in simple harmonic oscillator functions. Because this ABM uses primitive basis functions centered in the arrangement channels, it gives a very compact representation at large ρ and, unlike the four other methods discussed, is more efficient at large ρ than at small ρ . Our calculations to date, ^{19,28} on systems as diverse as FH₂, $t\mu D_2$, LiFH, and HO₂, indicate that, for all atommolecule systems, it is much more efficient than the previous four methods at large ρ and that, for systems such as²⁸ LiFH, it is more efficient than any of the other methods at all o.

We have mentioned this ABM in publications,^{14(b),15} used it in calculations,^{19,28} and talked about it at meetings, and that has inspired other work and a publication³¹ along this line, but this paper contains the first detailed description of the method. In the next section we describe the method in detail including the boundary conditions, basis functions, matrix elements, and future refinements. Section III contains some example calculations to show how well the method works and to compare speed, convergence, etc., with other methods for surface function determination. Section IV contains discussion and conclusions.

II. THEORY. ANALYTIC BASIS METHOD

A. Surface function equation in APH coordinates

We have elsewhere⁶ presented a detailed reactive scattering theory formulated in adiabatically adjusting principal axes hyperspherical (APH) coordinates and will attempt here to only repeat essentials. In this approach, one needs adiabatic basis functions Φ of the APH hyperangles, and in this work we choose the Φ to satisfy the equation

$$\begin{bmatrix} T_h + \frac{15\hbar^2}{8\mu\rho^2} + C\hbar^2\Lambda^2 + V(\rho,\theta,\chi_i) - \mathscr{C}^p_{t\Lambda}(\rho) \end{bmatrix} \times \Phi^p_{t\Lambda}(\theta,\chi_b\rho) = 0, \qquad (1)$$

where

$$T_{h} = \frac{-\hbar^{2}}{2\mu\rho^{2}} \left[\frac{4}{\sin 2\theta} \frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^{2}\theta} \frac{\partial^{2}}{\partial\chi_{i}^{2}} \right]$$
(2)

is the "hyperspherical" part of the kinetic energy operator, and

$$C = \frac{1}{\mu \rho^2 (1 - \sin \theta)} \tag{3}$$

is part of the centrifugal potential. V is the whole potential energy surface (PES), and the \mathscr{C} are the eigenenergies. The variable θ is the APH bending angle; its range is $0 \le \theta \le \pi/2$, with $\pi/2$ describing linear configurations and 0 describing triangular symmetric top configurations. χ_i is the APH kinematic angle measured from the "incident" arrangement channel; it measures motion between arrangement channels, and its range is $-\pi \leq \chi_i \leq \pi$. The angles θ and χ_i cover the upper half of the surface of an internal coordinate sphere which we loosely call the "hypersphere." (Strictly, the surface of the hypersphere is the 5D space covered by θ , χ_i , and the three Euler angles which describe the orientation of the principal axes in space.)

As one can see from Eq. (1), the surface functions Φ and eigenenergies \mathscr{C} depend parametrically on the hyperradius ρ . They are needed at a set of ρ values $\{\rho_{\xi}\}$, $\xi = 1, 2, \dots n_{\rho}$, which span the range of ρ values needed. ρ_{F} defines the center of the sector on which the functions $\Phi(\theta, \chi_b \rho_{\ell})$ are used as basis functions. The $15\hbar^2/8\mu\rho^2$ term in Eq. (1) comes from removal of first derivative terms from the coupled channel (CC) equations; it is a constant in this equation and can be folded into the $\mathscr C$ if desired. \hbar (Planck's constant divided by 2π) is unity in atomic units, and μ is the three-body reduced mass of the system arising from mass-scaled coordinates.⁶ The three quantum numbers labeling the \mathscr{C} and Φ are Λ , which is the component of the total angular momentum along the APH body-frame (BF) z axis (the axis of least inertia of the three-body system), the parity $(-1)^p$, with p=0 or 1, of Φ under $\chi_i \rightarrow \chi_i \pm \pi$, and $t=1,2,...,n_{\Phi}$, which just indexes the solutions in energy order.

We note that Eq. (1) differs from Eq. (164) of Ref. 6 slightly because it omits a rotational term of the form $\frac{1}{2}(A)$ $+B)\hbar^{2}[J(J+1)-\Lambda^{2}]$. As pointed out by Launay and LeDourneuf,^{2,12} this omission gives surface functions Φ which are independent of the total angular momentum J.

so that many fewer surface functions must be calculated. The omitted term is easily included in the CC equations along with the related Coriolis and asymmetric top terms.⁶ This surface function basis is expected⁷ to produce rapid convergence of the CC expansion to the exact solution provided triangular symmetric top ($\theta = 0$) configurations are unimportant, and this is the case in many reactions.

The boundary conditions on the Φ are that they be continuous functions of χ_i at $-\pi$ and π and regular everywhere.⁶ For systems with two or three identical atoms, the surface functions have other symmetries in addition to the parity p already defined.

The surface functions are real and normalized according to⁶

$$\int_{-\pi}^{\pi} d\chi_i \int_{0}^{\pi/2} \sin 2\theta \, d\theta \, \Phi_{t'\Lambda}^{p'}(\theta, \chi_{\dot{b}}\rho) \Phi_{t\Lambda}^{p}(\theta, \chi_{\dot{b}}\rho)$$
$$= \delta_{t't} \delta_{p'p}. \tag{4}$$

B. Surface function equation in Delves coordinates

We wish to express the surface functions as a basis set expansion of the form

$$\Phi^{p}_{t\Lambda} = \sum_{f} \mathscr{F}^{p\Lambda}_{f}(\theta, \chi_{ij}\rho) A_{ft}, \qquad (5)$$

where the coefficients A_{ft} are to be determined by the variational principle. We center the functions in the arrangement channels, so that $f = (\tau_f, v_f, j_f)$ is a composite index labeling the arrangement channel τ , vibrational quantum number v, and rotational quantum number j, respectively. For notational brevity, f will be used to represent *any* or all of these indices.

The simplest way we know to get functions $\mathcal F$ centered in the arrangement channels is to express them in the Delves hyperspherical coordinates, ${}^{32}\vartheta_f$ and Θ_f , where ϑ_f relates the lengths of the two scaled Jacobi vectors in the τ_f th arrangement and Θ_f is the angle between the two Jacobi vectors of the τ_f th arrangement channel. However, Delves coordinates cover configuration space only once, and the functions $\mathscr{F}_{f}^{p\Lambda}$ must have good parity p under $\chi_i \rightarrow \chi_i \pm \pi$, which makes use of the fact that the APH coordinates cover configuration space twice. To obtain this parity simply, we take

$$\mathscr{F}_{f}^{p\Lambda}(\theta,\chi_{i;\rho}) = \cos^{p}\chi_{f}F_{f}^{\Lambda}(\vartheta_{f},\Theta_{f};\rho), \qquad (6)$$

where F is a function only of the Delves angles of arrangement τ_f , and χ_f is given by⁶

$$\chi_f = \chi_i - \chi_{fi}, \qquad (7)$$

where χ_{fi} , the kinematic angle between arrangements τ_f and τ_i , is a known constant that depends only on the masses of the particles.⁶ If the parity is even (p=0), the cosine factor in Eq. (6) is simply unity; if the parity is odd (p=1), the cosine assures the correct parity but is still near unity near arrangement channel τ_{f} .

To see what functions to use for the F in Eq. (6), we express the operator T_h of Eq. (2) in the Delves angles of the τ_f th arrangement. This can be done in several ways; a

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straightforward but tedious way is to use the chain rule and the expressions for the Delves angles in terms of the APH angles,⁶

$$\tan \vartheta_{f} = \left[\frac{1 - \sin \theta \cos 2\chi_{f}}{1 + \sin \theta \cos 2\chi_{f}}\right]^{1/2},$$
$$\cos \Theta_{f} = \frac{\sin \theta \sin 2\chi_{f}}{\left[1 - \sin^{2} \theta \cos^{2} 2\chi_{f}\right]^{1/2}},$$
(8)

and their inverses,

$$\tan \theta = \frac{\left[\cos^2 2\vartheta_f + \sin^2 2\vartheta_f \cos^2 \Theta_f\right]^{1/2}}{\sin 2\vartheta_f \sin \Theta_f},$$

$$\sin 2\chi_f = \frac{\sin 2\vartheta_f \cos \Theta_f}{\left[\cos^2 2\vartheta_f + \sin^2 2\vartheta_f \cos^2 \Theta_f\right]^{1/2}},$$
(9)

$$\cos 2\chi_f = \frac{\cos 2\vartheta_f}{[\cos^2 2\vartheta_f + \sin^2 2\vartheta_f \cos^2 \Theta_f]^{1/2}}.$$

The result is

$$T_{h} = \frac{1}{2\mu\rho^{2}} \left[\frac{-\hbar^{2}}{\sin^{2}2\vartheta_{f}} \frac{\partial}{\partial\vartheta_{f}} \sin^{2}2\vartheta_{f} \frac{\partial}{\partial\vartheta_{f}} + \left(\frac{1}{\cos^{2}\vartheta_{f}} + \frac{1}{\sin^{2}\vartheta_{f}} \right) \mathscr{L}^{2} \right],$$
(10)

where \mathscr{L}^2 given by

$$\mathscr{L}^{2} = -\frac{\hbar^{2}}{\sin\Theta_{f}}\frac{\partial}{\partial\Theta_{f}}\sin\Theta_{f}\frac{\partial}{\partial\Theta_{f}}.$$
 (11)

Equation (10) can be checked simply^{30,33} [cf. Eq. (27) of Ref. 6] by noting that it is the J=0 limit of the square of Smith's grand angular momentum³⁴ operator.

It should be noted that the sum in Eq. (5) runs over all three arrangement channels in general, and when Eq. (10) is substituted for T_h in Eq. (1) to act on functions centered in a particular arrangement τ_f , the remainder of Eq. (1) remains unchanged; i.e., the BF axes are still the APH axes.

In choosing the basis functions F, we only need require that they have the important features of the exact solutions, so that we can proceed by a series of approximations. For example, we want the primitive basis to be compact at large ρ and well behaved at all ρ , and that requires consideration of the boundary conditions. At large ρ , in the region localized near arrangement channel τ_f , the potential V becomes, to within an additive constant, the diatomic vibrational potential $v_f(s_f) = v_f(\rho \sin \vartheta_f)$, which is independent of Θ_f and dependent only on the mass-scaled internuclear distance s_f of the diatomic molecule of the τ_f th arrangement. Because three-body terms in the potential are very system dependent, we only attempt to make the basis functions in arrangement f depend directly on the twobody potential v_f of that arrangement. Thus, we consider Eq. (1) with V replaced by v_f and T_h given by Eqs. (10) and (11). We then note that the C of Eqs. (1) and (3) is singular at all linear configurations and use Eq. (9a) to write

$$\sin \theta = [\cos^2 2\vartheta_f + \sin^2 2\vartheta_f \cos^2 \Theta_f]^{1/2}$$
$$= [1 - \sin^2 2\vartheta_f \sin^2 \Theta_f]^{1/2}.$$
(12)

At very large ρ , ϑ_f becomes small for all configurations near the minimum of $v_f(\rho \sin \vartheta_f)$. For such configurations and also when ϑ_f is near its other extreme of $\pi/2$, or whenever Θ_f is near its extremes of 0 or π , Eq. (12) can be expanded to give C of Eq. (3) as

$$C \approx \frac{4}{2\mu\rho^2 \sin^2 2\vartheta_f \sin^2 \Theta_f}.$$
 (13)

Noting that

$$\frac{1}{\cos^2\vartheta_f} + \frac{1}{\sin^2\vartheta_f} = \frac{4}{\sin^22\vartheta_f},$$
(14)

one sees that the factor multiplying the \mathcal{L}^2 in Eq. (10) also occurs in Eq. (13). Thus, some simple basis functions which will remove all the singularities in Θ_f are the associated Legendre polynomials, i.e., the familiar body-frame (BF) diatomic rotational functions.

To see the behavior that the vibrational functions need to have, we let

$$F_{f}^{\Lambda}(\vartheta_{f},\Theta_{f};\rho) = \frac{\Upsilon_{f}(\vartheta_{f};\rho)}{\sin 2\vartheta_{f}} \hat{P}_{j_{f}\Lambda}(\Theta_{f}), \qquad (15)$$

where the circumflex on the associated Legendre polynomial P implies normalization to unity, and we substitute one term of Eq. (5) into Eq. (1), ignoring the $\cos^{p} \chi_{f}$ term since it is near unity in arrangement f at large ρ . The resulting equation is

$$\begin{bmatrix} -\hbar^2 \\ 2\mu\rho^2 \\ \partial\vartheta_f^2 \end{bmatrix} + v_f(\rho\sin\vartheta_f) - \epsilon_f(\rho) \end{bmatrix} \Upsilon_f(\vartheta_f;\rho) = 0,$$
(16)

where ϵ should approximate one of the \mathscr{C} at large ρ to within an additive constant stemming from the choice of the zero of V.

Because \mathcal{F} and F, like Φ , must be regular everywhere, it is clear from the denominator in Eq. (15) that Υ is required to vanish at least as fast as $\sin 2\vartheta_f$ at both ends of the range of ϑ_f . If j_f is nonzero in Eq. (16), it must vanish as fast as $\sin^{j+1} 2\vartheta_f$.

Clearly, there are many possible choices for the Υ basis. Here we elect to use the simple analytic functions described in the next subsection.

C. Harmonic functions of an anharmonic variable

For molecular systems the variable ϑ_f describes what is basically a vibrational motion, and one might think to use common vibrational functions such as simple harmonic oscillators or Morse oscillators, centered about the equilibrium angle of v_f , as an analytic basis for Eq. (16). However, ϑ_f runs over the *finite* range 0 to $\pi/2$. At large ρ , $v_f(\rho \sin \vartheta_f)$ becomes essentially asymptotic by $\vartheta_f = \pi/2$, and such oscillator functions essentially vanish by $\pi/2$; however, at small ρ , v_f is far from asymptotic at $\vartheta_f = \pi/2$, and they do not satisfy the boundary condition at $\pi/2$.

Furthermore, neither harmonic nor Morse oscillators exactly vanish at $\vartheta_f = 0$ ($s_f = 0$). For some molecules this is not a problem in practice, but for many molecules, large order Gauss-Hermite quadratures then use points that reach or even go beyond the singularity in v_f at $s_f=0$ into the unphysical region where $s_f < 0$ and $\vartheta_f < 0$ and produce divergences. To avoid these problems, we choose the following basis:

$$\frac{\Upsilon_f(\vartheta_f;\rho)}{\sin 2\vartheta_f} \approx \frac{1}{B_f(\vartheta_f)} \phi_{\nu_f}(z_f), \tag{17}$$

where ϕ is a simple harmonic oscillator function of z_f ,

$$\phi_{\nu_f}(z_f) = \frac{1}{\left[\pi^{1/2} 2^{\nu_f}(\nu_f!)\right]^{1/2}} H_{\nu_f}(z_f) e^{-z_f^2/2}, \tag{18}$$

 H_{v_f} is a Hermite polynomial, and B_f is a factor to simplify the Jacobian for ϕ normalized on z_f . z_f is chosen to be

$$z_f = a_f \tan \vartheta_f - \frac{b_f}{\tan \vartheta_f} + c_f.$$
⁽¹⁹⁾

This choice assures that, so long as $a_f > 0$ and $b_f > 0$, z_f runs from $-\infty$ to ∞ as ϑ_f runs from 0 to $\pi/2$, and ϕ_{v_f} vanishes exactly at both ends of the range at all ρ . Furthermore, because it vanishes exponentially rather than simply as a power of $\sin 2\vartheta_f$, it removes the singularities for all j_f , and this allows the simplification of taking the ϕ basis independent of j_f . With the three coefficients in Eq. (19) one has enough freedom to match the equilibrium position, fundamental frequency, and anharmonicity desired for Υ as will be shown. That is why we call z_f an "anharmonic" variable. Also, we note that inversion of Eq. (19) simply requires solution of a quadratic equation in tan _d.

To determine the factor B_{f} , we note that, in any given calculation, all the basis functions used have the same parity (p'=p), and one can show⁶ that the two halves of the integration over χ_i in Eq. (4) add constructively. Thus, the integral over a pair of the basis functions of Eq. (5),

$$I = \int_{-\pi}^{\pi} d\chi_i \int_{0}^{\pi/2} \sin 2\theta \, d\theta \, \mathscr{F}_{f'}^{p\Lambda} \mathscr{F}_{f}^{p\Lambda}, \tag{20}$$

becomes⁶

$$I = 4 \int_{0}^{\pi/2} \sin^{2} 2\vartheta_{f} d\vartheta_{f} \int_{-1}^{1} d\cos \Theta_{f}$$
$$\times \cos^{p} \chi_{f'} \cos^{p} \chi_{f} F_{f'}^{\Lambda} F_{f}^{\Lambda}.$$
(21)

At large ρ , for two functions in the same arrangement channel $(\tau_{f'} = \tau_f)$, the parity factor stays unity over the range where the basis functions are nonzero. Using Eqs. (15) and (17) one obtains

$$I = \delta_{j'_f j_f} 4 \int_0^{\pi/2} \sin^2 2\vartheta_f \, d\vartheta_f \, \frac{1}{B_f^2(\vartheta_f)} \, \phi_{\nu'_f}(z_f) \phi_{\nu_f}(z_f).$$
(22)

Changing to z_f as the variable of integration and choosing B_f to be

$$B_f(\vartheta_f) = \frac{\sin^2 2\vartheta_f}{[a_f \sin^2 \vartheta_f + b_f \cos^2 \vartheta_f]^{1/2}},$$
 (23)

one obtains

$$I = \delta_{j'_f j_f} \int_{-\infty}^{\infty} dz_f \, \phi_{\nu'_f}(z_f) \phi_{\nu_f}(z_f) = \delta_{j'_f j_f} \delta_{\nu'_f \nu_f}.$$
 (24)

This choice of functions and factors to make the primitive basis orthonormal at large ρ is not necessary, but it is helpful in debugging programs.

D. Choice of parameters

The ϕ basis just introduced can be no better than its parameters, a_f , b_f , and c_f . If they are well chosen, the basis is expected to be compact and efficient; if not, it will be a poor basis. One could determine these parameters by direct nonlinear least squares minimization of the surface function eigenvalues at a number of values of ρ , but these parameters vary over a wide range as ρ varies over its range, so that such an approach is expected to be tedious and expensive. In the Appendix we show how to simply get good initial estimates for the values of the parameters a_f , b_f , and c_f of z_f by choosing the functions ϕ to behave approximately like Morse eigenfunctions. Then, final values of the parameters can be determined by variational scaling of the model Morse potential parameters to make the basis set used as accurate as possible.

E. Matrix elements and secular equation

Let us now consider use of this analytic basis to determine the surface functions Φ . The basis is in the form

$$\mathscr{F}_{f}^{p\Lambda}(\theta, \chi_{ij}\rho) = \cos^{p} \chi_{f} \frac{1}{B_{f}(\vartheta_{f})} \phi_{\nu_{f}}(z_{f}) \hat{P}_{j_{f}\Lambda}(\Theta_{f}).$$
(25)

As noted already, this set of basis functions is orthonormal at large ρ . As ρ shrinks and the functions centered in different arrangement channels begin to overlap, the functions with even parity (p=0) remain normalized and orthogonal to the other functions in the same arrangement but not orthogonal to the basis functions in the other arrangement channels. Basis functions with odd parity (p=1) slowly become unnormalized and nonorthogonal within the same arrangement as well as nonorthogonal to the functions in the other arrangements.

The matrix elements of the Hamiltonian of Eq. (1) needed to construct the secular equation can be calculated in several ways. At moderately large and large ρ it is convenient to use Delves coordinates and equations analogous to Eqs. (21) through (24) and evaluate the integrals using Gauss-Legendre quadrature in $\cos \Theta_f$ and Gauss-Hermite quadrature in z_f . Each basis function \mathcal{F} is constructed at the points of the quadratures centered in all three arrangements, and the quadrature then quickly runs over the points needed. When both basis functions are in the same arrangement channel, this provides a highly optimized and efficient quadrature. If the two functions are in different arrangement channels $(\tau_{f'} \neq \tau_f)$, the quadratures are car-

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ried out separately in the two arrangements and the results compared to check for convergence. In this case the Jacobian B_f factors do not all cancel, and the quadratures are clearly not optimum, but they converge well in practice when the overlaps between different arrangements are not too large.

At small and moderate values of ρ the overlaps between functions in different arrangements become large, and it becomes more efficient to use APH coordinates and to quadrature integrals analogous to Eq. (20). We have used a Gauss-Legendre quadrature in cos 2θ and have broken the χ_i integration up into as many as 7 Gauss-Legendre quadratures to allow concentration of the points in regions desired. In this process, the parities of the functions are invoked, and one only need integrate over half of the χ_i range.

In evaluating the kinetic energy integrals, particularly when the two basis functions are centered in different arrangements, we have found it convenient to start with T_h in APH coordinates as in Eq. (2), integrate by parts so that only first derivatives are involved, and then use Eq. (8) and the chain rule to express those first derivatives in terms of derivatives with respect to the coordinates of the basis function on which they act.

Because the APH coordinates treat all the particles equivalently, the symmetries are simple and apparent when two or more of the particles are identical. In such a case linear combinations of the primitive basis which transform as the irreducible representations of the symmetry group are used, and this markedly reduces the total number of basis functions needed. It also markedly reduces the number of quadrature points needed in performing the integrals as the quadratures then need cover only a small part of the χ space.

Because the basis is not orthogonal in general, it is necessary to solve a generalized eigenvalue problem. We use symmetric orthogonalization to diagonalize the overlap matrix. Then, to avoid linear dependence problems, any of the new (transformed) basis functions that have overlap eigenvalues less than 10^{-6} are discarded. The Hamiltonian matrix is then transformed to the new basis and diagonalized to give the surface functions and their eigenvalues. Thus far, the basis has proved so efficient that the matrices have been small enough to be directly diagonalized by efficient system subroutines; however, iterative diagonalization methods could be used whenever needed.

The other matrix elements discussed in Ref. 6 that are needed to carry out reactive scattering calculations, such as the rotational, asymmetric top, and Coriolis coupling terms as well as the sector to sector overlaps, are assembled from integrals over the primitive basis functions, and these are evaluated in the same way as the matrix elements just discussed.

F. Future improvements

The above analysis immediately suggests several possible improvements which we have not yet implemented but which might make this analytic basis method (ABM) even more accurate and efficient. The first is basis set contraction. One could use the asymptotic vibrational functions resulting from the present calculations at large ρ to contract the vibrational basis. Further, the current \hat{P} rotational basis could be replaced by hindered rotor functions. One could also use the surface functions determined at some finite ρ as a contracted basis for neighboring values of ρ . Thus far, we have kept the full basis for completeness.

A second improvement, noted in the Appendix, would be to actually use odd- ν oscillators centered at $\pi/2$ at small ρ . This would probably speed convergence for insertion reactions where ϑ_f near $\pi/2$ plays a very important role. Such oscillators could vanish there at the precise rate needed (as $\sin^{j+1} 2\vartheta_f$) whereas the present basis functions vanish more rapidly.

A third improvement, which should speed convergence for extremely anharmonic molecules such as $t\mu D$, would be to replace the z_f of Eq. (19) by

$$z_f = a_f \tan^{1/2} \vartheta_f - \frac{b_f}{\tan^{1/2} \vartheta_f} + c_f.$$
(26)

This choice corresponds closely to one of Schwenke;³¹ it should give functions which behave more like Morse functions at large ϑ_f when ρ is large than do the present basis functions.

A fourth variation that might lead to improvement is the following: The surface functions are presently used as a "sector-adiabatic" basis in the scattering calculations; i.e., they are calculated at the center of each propagation center and then taken to be independent of ρ on that sector. Because of the simplicity of the present basis and its essentially analytic dependence on ρ , it should be possible to treat it as a truly adiabatic basis. Then, as ρ grows, the shrinkage of the arrangement channels in hyperspherical coordinates would be automatically included in the basis, overlaps between sectors would be unnecessary, and the surface functions would need to be evaluated at fewer values of ρ . However, first derivatives with respect to ρ would then appear in the coupled equations which would slow the propagation. It might be possible to remove them via an adiabatic to diabatic transformation;³⁵ however, it is not yet clear whether this approach would work well enough to produce a real increase in efficiency.

The final variation that we mention concerns Coulombic systems. The present basis is appropriate for atomdiatom systems. For a system composed of charged particles, such as e^+ +H, a basis that behaves more like Coulomb or Sturmian wave functions will produce more rapid convergence than the present oscillator basis.

III. EXAMPLE CALCULATIONS AND RESULTS

In this section we report the results of ABM calculations of surface functions and compare them with the results of the DVR and FEM methods. The system chosen as a nontrivial example is the $F+H_2 \rightarrow HF+H$ reaction; its treatment requires generation of a large basis of surface functions. The potential energy surface (PES) used is the one of Brown *et al.*³⁶ commonly called the T5A surface, and we choose the zero of energy to be at the bottom of the

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TABLE I. Input parameters for the $F+H_2$ ABM calculations.

Arrangement	1 2 and	
Atomic mass (amu)	18.998 403 2	1.007 825 03
Scale factor d	1.379 008 1	1.000 635 4
ω _e (a.u.)	2.005 34(-2) ^a	1.885557(-2)
$\omega_e x_e$ (a.u.)	5.528 47(-4)	4.095 2(-4)
$r_e(a_0)$	1.401 12	1.732 517
v _{max}	3	7
j _{max}	12	31
nhermt	14 (11) ^b	18 (15)
nglegn	38 (16)	45 (35)

This notation implies 2.005 34×10^{-2} .

^bQuadrature size at small and large ρ .

asymptotic HF potential wells. This PES has been used in many calculations^{2,3,8,22,37–39} on this reaction, and plots of the PES and surface functions showing their appearance in APH coordinates have also been published.^{15,17(b)} Arrangement 1 or i (initial) is that of the $F+H_2$ reactants.

The calculations are for $\Lambda=0$ and even parity (p=0)and include all functions connecting to the even j rotational states of the F+H₂ arrangement. Because of the symmetry due to the identical H atoms, this only requires including in the ABM calculations the even j rotational functions of H₂ and the linear combinations of HF functions that are even under reflection about $\chi_i=0$.

Table I gives the values of some input parameters. The mass of the atom in each arrangement is given in atomic mass units, and the dimensionless mass-scaling factors are also given. The spectroscopic parameters are those of Huber and Herzberg⁴⁰ expressed in hartree atomic units. The ABM harmonic oscillator basis included vibrational quantum numbers from zero up through the v_{max} shown, and the rotational basis functions with *j* running from zero up through the j_{max} shown were included with each v. With symmetry, this gives a total of 284 primitive vibration–rotation basis functions; without symmetry, this number would double.

The calculations were performed at five representative ρ values ranging from the smallest to the largest values needed in our reactive scattering calculations.^{8,22} The precise values of ρ chosen have no particular meaning, and some were chosen simply because the convergence of the DVR method had already been studied there.⁸

The quadratures at the two shortest ρ values were performed in the APH space. The θ quadrature was broken up into two segments, with 14 points between 0 and 0.65 rad and 32 points between 0.65 and $\pi/2$ radians. With symmetry, integration over only one fourth of the χ_i range is required, and this quadrature was broken up into four segments, with the 11 positive points of a 22 point quadrature between 0 and 0.2, 16 points between there and 0.49, 44 points between there and 1.18, and 18 points between there and $\pi/2$ radians. This gives a total of 4094 quadrature points.

At the third value of ρ the calculations were performed both with this APH quadrature and also with quadratures in the arrangement channel Delves' angles using the larger

TABLE II. Variational parameters for the F+H₂ ABM calculations.

Arrangement	1 2 an	
r _x	1.086	1.036
ca	0.923	0.917
a_n	0.85	1.14
ζ	0.1	1.0
δ	0.01	0.01
$s_m = r_x r_e/d$	1.103 41	1.793 748

numbers of Hermite and Legendre quadrature points shown in the lower part of Table I; with symmetry that produces a total of 1076 quadrature points. At the largest two ρ values arrangement channel quadratures with the smaller numbers of points shown in parentheses in the lower part of Table I were used; with symmetry that produces a total of 613 points.

All these quadratures are chosen to give convergence with respect to quadrature that is at least one and often two significant figures more accurate than the convergence expected of the energies. This assures that the parameters can be varied and optimized to minimize the energies. If poorly converged quadratures are used, the calculated energies often lie below their converged values, and any nonlinear variation of parameters simply moves in the direction that makes the quadrature diverge and give spurious energy eigenvalues. For production work, one could probably use fewer quadrature points and gain some speed; however, that was not done here, and all the ABM energies presented are true variational upper bounds.

To optimize this basis for the actual PES used, we proceeded as follows: The scaling factors shown in Table II were introduced into the calculation, with r_x scaling the equilibrium internuclear distance used to determine the basis, c_{α} scaling the right-hand sides of Eqs. (A11) and (A12), and a_n scaling the second term in the parentheses on the right-hand sides of Eqs. (A11) and (A12). With this choice c_{α} essentially scales the frequency of the oscillators, and a_n essentially scales the anharmonicity. The values of these three parameters listed in Table II were determined by nonlinear least squares minimization of the average of the first nine vibrational energies at a large value of ρ (100 a_0). This assures good asymptotic energies for all the open and at least one closed vibrational state in each arrangement channel at the highest energies used in the scattering calculations.^{8,22}

These variational calculations are easily carried out because the rotational basis is exact at large ρ , and the calculations need only be done with the vibrational basis, that is, with $j_{max}=0$ in all arrangements. With symmetry, that is a basis of only 12 functions, 4 in the H₂ arrangement and 8 in the HF arrangements. The asymptotic energies of the seven-vibrational states that are ever open in our calculations are listed in Table III and compared there with the results of calculations in Jacobi coordinates that used a large harmonic oscillator basis with 30 oscillators in each arrangement channel. One sees there that the harmonic functions of an anharmonic variable are forming an excel-

TABLE III. Asymptotic energies \mathscr{C} in eV for the rotationless (j=0) vibrational states v. See the text for discussion.

Fragment	ν	ABM	Large basis
HF	0	0.253 87	0.253 87
HF	1	0.745 50	0.745 50
HF	2	1.215 62	1.215 62
H_2	0	1.645 33	1.645 26
HF	3	1.664 30	1.664 24
HF	4	2.091 63	2.091 36
H_2	1	2.159 37	2.158 92

lent but very compact basis. The lower vibrational states all have energies accurate to 0.01 meV, and the highest states are accurate to within 0.5 meV. We note that the values shown are actually those at $\rho = 1000 a_0$; at smaller but still asymptotic values of ρ , the hyperspherical vibrational energies are slightly lower than the Jacobi energies due to the curvature of the surface of the hypersphere.

The calculations at large ρ are not sensitive to the values of the variational parameters ζ and δ of Eqs. (A8) and (A9). These were determined by nonlinear least squares variation of the average energy at the smallest value of ρ needed (2.2 a_0). Because this value is significantly larger than the larger of the scaled equilibrium distances shown in Table II, this system never encounters the $\rho < s_{mf}$ range of discussed in the Appendix, the results are never very sensitive to these two parameters, and a few calculations with the full basis suffices to give the values shown in Table II.

The method and code used for the symmetry-adapted DVR calculations were described in detail in an earlier publication.⁸ The parameters used are given in Table IV. The parameters l_{max} and m_{max} give the number of DVR points in the θ and χ directions, respectively. V_{max} and E_{cut} are the potential and eigenvalue cutoffs used in the sequential diagonalization-truncation procedure.

The FEM code used the same meshing technique as described before^{6,15} to produce a highly nonuniform grid that is coarse where the wave functions are small and fine where they are large. However, the Hamiltonian matrix was diagonalized with the spectral transform Lanczos method^{19,20} (STLM). As we noted in Sec. I, the STLM is a full order of magnitude faster than the subspace iteration and block Lanczos diagonalization methods tried earlier,^{17,18} and that allows the present FEM calculations to be performed on a SUN Sparc 2 workstation in about the same time as the earlier methods would have required on a CRAY-XMP. In these calculations the tolerance parame-

TABLE IV. Parameters used in the DVR calculations.

ρ (a_0)	l _{max}	m _{max}	$V_{\rm max}({\rm eV})$	$E_{\rm cut}({\rm eV})$
2.2	30	60	30.0	25.0
3.037 582 8	30	60	20.0	10.0
4.974 796 6	40	60	7.0	4.0
7.298 999 3	50	80	7.0	4.0
9.0	50	100	7.0	4.0

TABLE V. ABM, DVR, and FEM surface function energies \mathscr{C}_i in eV, average energies, dimension of eigenvalue equations, and cpu times at $\rho=2.2 a_0$. See the text for discussion.

t	ABM	DVR	FEM
1	6.9177	6.9177	6.9177
2	7.0341	7.0341	7.0342
3	7.1298	7.1296	7.1299
4	7.3042	7.3038	7.3043
5	7.4932	7.4927	7.4933
6	7.7007	7.7008	7.7009
7	7.9219	7.9202	7.9222
8	8.0789	8.0786	8.0791
9	8.1524	8.1475	8.1529
10	8.2502	8.2494	8.2503
8 (10)	7.5983	7.5974	7.5985
N	271	617	3047
cpu(min)	22.8	10.4	12.6

ters were chosen to give eigenvalues of approximately the same quality as those given by the current ABM and DVR calculations, and five point Gaussian quadratures were used to assure that the results were variational upper bounds to the true energies.

The results are given in Tables V through IX for the five values of ρ chosen. In each the energy eigenvalues of the highest ten important or open surface function states are given in eV. The omitted lower eigenvalues always agree even better than those shown. Also shown is $\overline{\mathscr{B}}(n)$, the average of the first n eigenvalues. This gives a convenient measure of the overall agreement of the methods. The quantity N is the dimension of the eigenvalue problem actually solved. In the ABM and DVR calculations the diagonalization was done directly using standard routines, so that all N eigenvalues and eigenfunctions were generated. In the FEM calculations the STLM routine was required to generate 150 eigenvalues and eigenfunctions because this number of coupled equations was propagated in the scattering calculations.⁸ The cpu times for a SUN Sparc 2 workstation to perform the complete calculation (setup, integrals, transformations, and diagonalization) are shown as the last line of each table.

The results at the shortest distance are in Table V. The agreement of the three methods is good. The 1 meV agreement of the average energies in this very repulsive region, where all the channels are strongly closed and very precise eigenvalues are not important, is more than accurate enough for any scattering calculations envisioned. At this ρ the DVR is the fastest of the three with the FEM a close second and the ABM taking about twice as much time as the DVR due to the large number of quadrature points required when the ABM integrals are done in the APH coordinates. At the second distance (Table VI) the accuracies are also all fully satisfactory with agreement being even better, namely, to within a few tenths of a meV. The relative efficiencies are about the same as at the first ρ value.

At the third distance (Table VII) the situation has changed. ABM calculations performed with both the APH and arrangement channel quadratures gave identical ener-

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TABLE VI. ABM, DVR, and FEM surface function energies &, in eV, average energies, dimension of eigenvalue equations, and cpu times at $\rho = 3.0375828 a_0$. See the text for discussion.

t	ABM	DVR	FEM	
11	1.9845	1.9845	1.9849	
12	1.9975	1.9975	1.9979	
13	2.0515	2.0515	2.0519	
14	2.1090	2,1090	2.1093	
15	2.1275	2.1275	2.1281	
16	2.1352	2.1353	2.1357	
17	2.1994	2.1994	2.1998	
18	2.2578	2.2578	2.2584	
19	2.2730	2.2730	2.2737	
20	2.3197	2.3197	2.3204	
8 (20)	1.8551	1.8551	1.8554	
N	277	653	3307	
cpu(min)	22.9	12.3	14.8	

gies to all figures shown. The ABM and DVR average energies agree to within 0.2 meV, and the individual energies, even for the higher states, usually agree to within about 1 meV, which is very good. It should be emphasized that the fact that the DVR energies often lie lower than the ABM energies does not mean that they are more accurate; the DVR method is not variational, and its higher eigenvalues often converge from below. We believe the ABM and DVR energies have about the same absolute accuracy here. The FEM gives an average energy which is about 1 meV high, and its higher energies are a few meV higher than the variational ABM energies. This ρ is in a region where flux piles up and resonances form. If one had narrow resonances whose energies were accurately needed, the FEM basis might not be quite adequate; however, it is still accurate enough for most scattering purposes. Looking at the times, we note that this ρ requires a fine grid over much of the angular space with the consequence that the DVR becomes about 50% less efficient than before, and the FEM becomes very inefficient. However, because the ABM can now use the arrangement channel quadratures, it be-

TABLE VII. ABM, DVR, and FEM surface function energies \mathscr{C}_t in eV, average energies, dimension of eigenvalue equations, and cpu times at $\rho = 4.9747966 a_0$. See the text for discussion.

t	ABM	DVR	FEM	
91	2.0564	2.0569	2.0679	
92	2.0754	2.0760	2.0928	
93	2.0981	2.0981	2.1023	
94	2.0990	2.0994	2.1141	
95	2.1098	2.1099	2.1148	
96	2.1196	2.1198	2.1278	
97	2.1273	2.1278	2.1443	
98	2.1542	2.1543	2.1537	
99	2.1551	2.1551	2.1608	
100	2.1602	2.1608	2.1621	
8(100)	1.3788	1.3790	1.3811	
N	284	665	4877	
cpu(min)	4.0	13.7	36.2	

TABLE VIII. ABM, DVR, and FEM surface function energies &, in eV,

average energies, dimension of eigenvalue equations, and cpu times at

comes the most efficient of the three, three times faster than the DVR and almost 8 times faster than the FEM.

At the fourth (Table VIII) and fifth (Table IX) distances the results are similar. Because the arrangement channels viewed in the hyperangles shrink as ρ grows, the angular region over which the fine grid is needed is a little smaller and the FEM and DVR methods a little less expensive than at the third distance. The ABM and DVR methods give excellent agreement. The FEM is less accurate and will not give thresholds that are very accurate. If the tolerances were set to make the FEM give results as accurate as the other two methods, it would markedly increase the time it requires, and it is already much the slowest of the three. The ABM is the most efficient of the three methods and a factor of 2 to 3 faster than the DVR.

For this FH₂ system, $\rho = 9.0 a_0$ is as large as distance as needed. However, many systems with strong long-range potentials and/or heavy-light-heavy atomic mass combinations require much larger distances to reach the asymptotic region. For example, the LiFH reaction²⁸ and the HO₂ reaction⁴¹ both need calculations out to ρ as large as 35 a_0 . To better understand what such systems would re-

TABLE IX. ABM, DVR, and FEM surface function energies \mathscr{C}_t in eV, average energies, dimension of eigenvalue equations, and cpu times at $\rho = 9.0 a_0$. See the text for discussion.

DVR 1 2.0701 4 2.0727	FEM 2.0720		ABM	DVR	FEM
1 2.0701 4 2.0727	2.0720				
4 2.0727		91	2.0747	2.0748	2.0805
	2.0760	92	2.0779	2.0782	2.0863
6 2.0869	2.0916	93	2.0964	2.0974	2.1051
1 2.0943	2.0961	94	2.1010	2.1009	2.1065
7 2.1093	2.1132	95	2.1153	2.1154	2.1233
2 2.1220	2.1267	96	2.1194	2.1197	2.1284
9 2.1495	2.1549	97	2.1252	2.1253	2.1315
0 2.1645	2.1672	98	2.1470	2.1482	2.1541
6 2.1799	2.1833	99	2.1545	2.1546	2.1562
2 2.1893	2.1918	100	2.1559	2.1560	2.1564
7 1.3975	1.3985	8 (100)	1.3791	1.3792	1.3812
721	5857	N	284	537	4617
16.6	10.7	· · · ·	4.0	0 7	
	2 2.1220 9 2.1495 0 2.1645 6 2.1799 2 2.1893 7 1.3975 721	2 2.1220 2.1267 9 2.1495 2.1549 0 2.1645 2.1672 6 2.1799 2.1833 2 2.1893 2.1918 7 1.3975 1.3985 721 5857 126 126	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22.12202.1267962.119492.14952.1549972.125202.16452.1672982.147062.17992.1833992.154522.18932.19181002.155971.39751.3985 $\overline{\mathscr{C}}$ (100)1.37917215857N284166166166166	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

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quire, we have performed ABM and DVR calculations for the present FH₂ example at $\rho = 35 a_0$. The ABM calculations were very simple, and the results are accurate and similar to those of Table IX: $\mathscr{C}(100)$ is 1.3801 eV, N is 284, and the calculation required 3.9 min of cpu time. However, the DVR proved quite unsatisfactory. With the 64 Mb of physical memory and 160 Mb of swap space that the SUN Sparc 2 workstation used has in its present configuration, the largest DVR parameters that could be used were $l_{\text{max}} = 100$ and $m_{\text{max}} = 200$. With these values and the other DVR parameters as at 9.0 a_0 , $\overline{\mathscr{C}}(100)$ is 1.5728 eV, which is in error by more than 190 meV, and the calculation required 29.9 min of cpu time. This markedly longer time is due to the much larger number of DVR points that must be handled; it is not because of the size of the final eigenvalue problem as N was only 189.

The DVR fails here because the arrangement channels are localized on a very small fraction of the angular space at large ρ , and the DVR points cover the whole space. Hence, it requires a huge number of DVR points to get the grid dense enough where points are needed to get convergence, and the rest of the points are wasted. To maintain convergence as ρ grows requires the parameters l_{max} and m_{max} to each grow proportional to ρ , so that the total number of DVR points grows as ρ^2 , and the memory requirements grow a little faster even than that. To obtain convergence at 35 a_0 would require an l_{max} near 200 and an m_{max} near 400, require five times as much memory as available, and run slowly. To avoid that would require significant alteration of the method and code.

On the other hand, to do ABM calculations at ρ equal to 35 or 100 or even 1000 a_0 is very simple and requires no changes of any of the basis parameters. The rotational basis becomes exact, the vibrational basis becomes optimized, and the channel quadratures become optimum. Hence, the ABM is ideally suited for calculations at large ρ .

IV. DISCUSSION AND CONCLUSIONS

In this paper we have presented an analytic basis method (ABM) for calculating the surface function basis needed in hyperspherical formulations of reactive scattering theory. Harmonic functions of an anharmonic variable were introduced and shown capable of providing a compact, efficient vibrational basis at all distances ρ .

Test calculations on the $F+H_2$ system with the T5A PES comparing the ABM, DVR, and FEM methods showed that the FEM method was always the least efficient of the three. Because the ABM basis is shaped by the potential, it always gave the most compact basis and required diagonalizing the smallest matrices of the three methods. At large ρ , where its quadrature is efficient, the ABM was the most efficient of the three methods. At small ρ , where the ABM quadratures were not efficient, the speed with which the DVR constructs the Hamiltonian matrix made it the most efficient method. Thus, for this system, the DVR is the method of choice for small ρ , and the ABM is the method of choice for large ρ . In fact, the present and other^{19,28,41} calculations indicate that the ABM method is

the method of choice at large ρ for all systems because the coverage of the whole space by the DVR points makes the DVR inefficient at large ρ .

As we show in future publications,^{19,28} it is easy to use one method at small ρ and switch over to another method at large ρ . In the present test system, such a combination of the DVR and ABM methods allows the surface function basis to be generated 50 times faster than in the earliest papers⁵⁻⁷ of this series. As a result, surface function calculations now consume only a small fraction of the computational effort in hyperspherical reactive scattering calculations.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy under the Laboratory Directed Research and Development program at Los Alamos National Laboratory.

APPENDIX: CHOOSING BASIS SET PARAMETERS

In this Appendix we show how to simply get good initial estimates for the values of the parameters a_f , b_f , and c_f of the anharmonic variable z_f of Eq. (19). We model the diatomic potential by a Morse potential and choose the functions ϕ to behave approximately like the Morse eigenfunctions Υ for the cases in which ρ is either larger or smaller than the position of the potential minimum.

To proceed, we assume that, as for most diatomic molecules, v_f behaves approximately like a Morse potential in the scaled Jacobi internuclear distance,

$$v_f(s_f) = D_f[e^{-2\beta_f(s_f - s_{mf})} - 2e^{-\beta_f(s_f - s_{mf})}], \quad (A1)$$

where s_{mf} is the position of the minimum, the equilibrium internuclear distance of the diatom of the τ_f th arrangement in the mass-scaled coordinates. Use of this Morse v_f should lead to basis functions with reasonable behavior at all distances except at such small ρ that the wave functions sense the failure of the Morse potential to have the correct singularity at $s_f=0$. Estimates of the depth D_f and steepness parameter β_f of this potential are obtained from the fundamental frequency ω_{ef} and anharmonicity $\omega_{ef} x_{ef}$ of the diatom via⁴²

$$\beta_f = \left(\frac{2\mu\omega_{ef} x_{ef}}{\hbar^2}\right)^{1/2},\tag{A2}$$

and

$$D_f = \frac{\omega_{ef}^2}{4\omega_{ef} x_{ef}}, \qquad (A3)$$

where all parameters are in some consistent set of energy and distance units such as atomic units, and μ is the threebody reduced mass.

Before continuing, we note that $s_f = \rho \sin \vartheta_f$ in Eq. (A1), and we consider the behavior of Eq. (A1) as a function of ϑ_f . This behavior is illustrated in Fig. 1, where a Morse potential is plotted as a function of ϑ_f for several values of ρ . At large ρ , v_f essentially reaches its asymptotic value as ϑ_f approaches its upper limit of $\pi/2$. At smaller



FIG. 1. Behavior of a Morse vibrational potential $v_f(s_f)$ as a function of the Delves angle ϑ_f at various values of the hyperradius ρ . The parameters are those for an HF fragment in the FH₂ system, but the qualitative behavior is the same for any vibrational potential. Note that the slope of the potential is always zero at $\vartheta_f = \pi/2$. (a) $\rho = 1.3 a_0$. The potential is similar to that of a simple but one-sided oscillator with its equilibrium position at $\vartheta_f = \pi/2$. (b) $\rho = 1.5 a_0$. The behavior is qualitatively the same as in (a). (c) $\rho = 1.793748 a_0$. Here $\rho = s_{mf}$, the scaled equilibrium distance. The potential is similar to that of a one-sided *quartic* oscillator with equilibrium position at $\vartheta_f = \pi/2$. (d) $\rho = 2.2 a_0$, the shortest distance needed in the scattering calculations. The potential appears very anharmonic and is far from reaching its asymptotic value at $\vartheta_f = \pi/2$. (e) $\rho = 3.0 a_0$. (f) $\rho = 5.0 a_0$. (g) $\rho = 7.3 a_0$. By this value of ρ , the potential is nearly harmonic near its minimum, has the classic diatomic potential shape, and essentially reaches its asymptotic value before ϑ_f reaches $\pi/2$.

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FIG. 1. (Continued.)

values of ρ , it does not reach its asymptote. However, because of the behavior of the sine function, it should be noted that the derivative of v_f with respect to ϑ_f is zero at $\pi/2$ at all ρ , and this behavior produces the following interesting phenomenon: When $\rho = s_{mf}$, v_f reaches its equilibrium position just as ϑ_f reaches its upper limit of $\pi/2$, and the two effects combine to make the first three derivatives of v_f vanish, so that v_f behaves like the potential of a quartic oscillator centered at $\pi/2$. For $\rho < s_{mf}$, v_f behaves like the potential of an ordinary oscillator centered at $\pi/2$.

The $\rho \geqslant s_{mf}$ case

Let us first consider the case in which $\rho \ge s_{mf}$. Then, the Delves angle of the minimum of v_f can be defined by

$$\vartheta_{mf} \equiv \sin^{-1}(s_{mf}/\rho). \tag{A4}$$

For convenience in what follows, we next approximate Eq. (A1) by a Morse potential in the Delves angle ϑ_f itself,

$$v_f(s_f) \approx D_f[e^{-2\gamma_f(\vartheta_f - \vartheta_{mf})} - 2e^{-\gamma_f(\vartheta_f - \vartheta_{mf})}].$$
(A5)

This replacement can be made in two ways: If one simply makes a small angle expansion of the sines in Eq. (A1), one obtains Eq. (A5) with

$$\gamma_f = \rho \beta_f; \tag{A6}$$

however, if one instead expands Eq. (A1) about ϑ_{mf} , one obtains Eq. (A5) with

$$\gamma_f = \rho \beta_f \cos \vartheta_{mf} \,. \tag{A7}$$

At large ρ the two expansions give the same result and are equivalent. For most ρ Eq. (A7) is more accurate than Eq. (A6). However, it should be noted that, at $\rho = s_{mf}$, where $\vartheta_{mf} = \pi/2$, an Eq. (A5) based on Eq. (A7) collapses and fails entirely for all ϑ_f . To allow the oscillators to spread out enough to be a good basis for the quartic oscillator at this ρ but to keep them from failing entirely, we mix Eqs. (A6) and (A7), choose γ_f to satisfy

$$\gamma_f = \rho \beta_f [\delta_f + (1 - \delta_f) \cos \vartheta_{mf}], \qquad (A8)$$

and determine the parameter δ_f variationally to give a good basis at $\rho = s_{mf}$ (or at the smallest ρ needed if that is larger than s_{mf}).

Using Eq. (A5) in Eq. (16), one can solve analytically⁴³ for the $j_f=0$ solutions. For the lowest solution, for use in Eq. (17) in determining the parameters of ϕ , we take

$$\Upsilon_{f} \approx e^{-\kappa_{f} \exp[-\gamma_{f}(\vartheta_{f} - \vartheta_{mf})]} e^{-\gamma_{f}(\kappa_{f} - 1/2)(\vartheta_{f} - \vartheta_{mf})} \times \cos^{\xi_{f}} \vartheta_{f}, \qquad (A9)$$

where κ_f is given by⁴²

$$\kappa_f = \frac{\omega_{ef}}{2\omega_{ef} x_{ef} [\delta_f + (1 - \delta_f) \cos \vartheta_{mf}]}.$$
 (A10)

The first two factors on the right side of Eq. (A9) simply constitute the ground state Morse oscillator wave function. The third factor enforces the $\pi/2$ boundary condition. Nominally, $\zeta_f \ge 1$; however, it turns out that any $\zeta_f \ge 0$ will lead to functions ϕ which vanish at $\pi/2$, so that we allow ζ_f to be a variational parameter which is determined at $\rho = s_{mf}$ or at the smallest ρ needed if that is larger than s_{mf} . For any ρ for which the Morse potential is reasonable, the Morse wave function Υ of Eq. (A9) decreases rapidly enough left of ϑ_{mf} that the resulting ϕ functions vanish rapidly at small ϑ_f without the complication of introducing an explicit sin ϑ_f factor in Eq. (A9).

We recall that Eq. (17) is

$$\frac{\Upsilon_f(\vartheta_f;\rho)}{\sin 2\vartheta_f} \approx \frac{1}{B_f(\vartheta_f)} \phi_{\nu_f}(z_f), \tag{17}$$

where B_f is simply the Jacobian factor, defined by Eq. (23), which makes the oscillator functions automatically orthonormal. To proceed, we use one factor of $\sin 2\vartheta_f$ out of the B_f in Eq. (17) to cancel the similar factor on the left-hand side of this equation. Then, we note that one can easily show that the rest of $1/B_f$ is, to within a constant factor, simply $(\partial z_f/\partial \vartheta_f)^{1/2}$. Since our objective here is to make the rapidly varying (exponential) parts of these functions match, we proceed as in the the usual theory of asymptotic expansions⁴⁴ to treat this preexponential factor as approximately constant.

Now, one can write the remaining functions in Eq. (17) as exponentials ($\phi = e^{-h}$ and $\Upsilon = e^{-g}$) and equate exponentials (ignoring arbitrary normalization factors). We denote the position of the maximum of ϕ and Υ , which is also the minimum of h and g, by ϑ_{Mf} and note that, because of anharmonicity, ϑ_{Mf} is not equal to ϑ_{mf} , the position of the minimum of the Morse potential. We note that h is simply $\frac{1}{2}z_f^2$ and g is the negative of the log of Eq. (A9) and expand both h and g in a power series in (ϑ_f) $-\vartheta_{Mf}$, equating terms through the cubic. After a little algebra involving the intermediate parameters $A = a_f \sec^2 \vartheta_{Mf}$ and $B = b_f \csc^2 \vartheta_{Mf}$, one finds that the desired parameters are given by

$$a_f = \cos^4 \vartheta_{Mf} \left(g_2^{1/2} + \frac{g_3}{6g_2^{1/2}} \tan \vartheta_{Mf} \right),$$
 (A11)

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$$b_f = \sin^4 \vartheta_{Mf} \left(g_2^{1/2} - \frac{g_3}{6g_2^{1/2}} \cot \vartheta_{Mf} \right),$$
 (A12)

$$c_f = b_f \cot \vartheta_{Mf} - a_f \tan \vartheta_{Mf}.$$
 (A13)

Here g_i is the *i*th derivative of g at ϑ_{Mf} . These are given by

$$g_2 = \gamma_f^2 \kappa_f e^{-\gamma_f(\vartheta_{Mf} - \vartheta_{mf})} + \zeta_f \sec^2 \vartheta_{Mf}, \qquad (A14)$$

and

$$g_3 = -\gamma_f^3 \kappa_f e^{-\gamma_f(\vartheta_{Mf} - \vartheta_{mf})} + 2\zeta_f \sec^2 \vartheta_{Mf} \tan \vartheta_{Mf},$$
(A15)

and ϑ_{Mf} is determined by the requirement that

$$g_1 = 0$$

= $-\gamma_f \kappa_f e^{-\gamma_f (\vartheta_{Mf} - \vartheta_{mf})} + (\kappa_f - \frac{1}{2})\gamma_f + \zeta_f \tan \vartheta_{Mf}.$
(A16)

Thus given any choice of the variational parameters δ_f and ζ_f , solution of this simple transcendental equation for ϑ_{Mf} determines the parameters a_f , b_f , and c_f which make the ϕ behave much like the appropriate Morse eigenfunction. The parameters adjust smoothly with ρ and are appropriate for all $\rho \ge s_{mf}$.

The *ρ*≤*s_{mf}* case

For many systems one never needs $\rho < s_{mf}$, and the above analysis suffices. However, when the diatomic molecule of one of the arrangement channels has a considerably longer bond length than one or more of the diatomics in the other arrangements in scaled Jacobi coordinates, it is often necessary to begin the propagation of the coupled channel (CC) equations at distances where $\rho < s_{mf}$ for the larger (longer) molecule.

For $\rho < s_{mf}$, one could probably get good accuracy and convergence using a harmonic oscillator basis in ϑ_f centered about $\pi/2$. However, that basis must include only the ϕ_{v_f} with odd integers v_f in order to satisfy the boundary conditions. It would also require integrating over half the usual range for harmonic oscillator variables. We have not yet implemented that approach as we have thus far been able to obtain rather good basis functions by a simple modification of the procedure used for $\rho \ge s_{mf}$. It keeps the same functions and variable ranges and proceeds as follows: Eq. (A1) is again approximated by a Morse potential in ϑ_f , which has the form of Eq. (A5), but now has

$$\vartheta_{mf} \equiv \pi/2.$$
 (A17)

The depth D_f of the Morse potential is again obtained from Eq. (A3). The steepness parameter γ_f is obtained by expanding Eqs. (A1) and (A5) in powers of $(\vartheta_f - \pi/2)$ and equating the first nonvanishing term (the quadratic). That gives

$$\gamma_f^2 = \beta_f \rho[u^2(\rho) - u(\rho)], \qquad (A18)$$

where

$$u(\rho) = e^{-\beta_f(\rho - s_{mf})},\tag{A19}$$

and the fact that $s_f = \rho$ at $\vartheta_f = \pi/2$ has been used.

While Eq. (A18) is expected to be satisfactory for most $\rho < s_{mf}$, the right-hand side vanishes at $\rho = s_{mf}$ for reasons already discussed. It also vanishes at extremely small ρ due to the factor of ρ on the right-hand side. This failure occurs because the Morse potential does not have the proper Coulomb singularity at zero internuclear distance. To join smoothly onto the parameters obtained for $\rho \ge s_{mf}$ and prevent failure at very small ρ , while approximating Eq. (A18) at most $\rho < s_{mf}$, we replace Eq. (A18) by

$$\gamma_f = \{ (\rho \beta_f \delta_f)^2 + \beta_f s_{mf} [u^2(\rho) - u(\rho)] \}^{1/2}.$$
 (A20)

With the parameters of the Morse potential thus chosen, one can again use Eq. (A9) with Eq. (A10) now replaced by

$$\kappa_{f} = \frac{\omega_{ef}\rho}{2\omega_{ef}x_{ef}\{(\rho\delta_{f})^{2} + (s_{mf}/\beta_{f})[u^{2}(\rho) - u(\rho)]\}^{1/2}},$$
(A21)

and proceed as before. For any $\zeta_f > 0$, the maximum of Υ_f and ϕ occurs at a ϑ_{Mf} , determined by Eq. (A16), which is less than $\pi/2$, and Eqs. (A11) through (A15) give a well behaved basis. The basis thus determined has proved satisfactory for $\rho < s_{mf}$ in all cases for which it has thus far been tested.¹⁹

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