

Symmetry-adapted distributed approximating functionals: Theory and application to the ro-vibrational states of H_3^+

Srinivasan S. Iyengar

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Gregory A. Parker

Department of Physics, University of Oklahoma, Norman, Oklahoma

Donald J. Kouri^{a)}

Department of Chemistry and Department of Physics, University of Houston, Houston, Texas 77204-5641

David K. Hoffman

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

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Symmetry-adapted Distributed Approximating Functionals (SADAFs) are derived and used to obtain a coordinate representation for the Adiabatically Aadjusting Pincipal Axis Hyperspherical (APH) coordinates kinetic energy operator. The resulting expressions are tested by computing ($J=0$) ro-vibrational states for the well-studied H_3^+ molecular ion system, by iterative diagonalization of the Hamiltonian matrix using the Arnoldi procedure. The SADAF representation and APH coordinate system are found to be computationally robust and accurate. © 1999 American Institute of Physics. [S0021-9606(99)01920-0]

I. INTRODUCTION

To obtain a numerical solution to either the time-dependent or the time-independent Schrödinger equation, it is necessary first to obtain a suitable basis, the projection onto which yields a representation for the Hamiltonian operator. Some of the popular choices for bases include the Fourier¹⁻⁴ functions, eigenstates for various bound degrees of freedom,⁵ and the discrete variable representation (DVR).^{6,7} In recent years, a new approach,⁸⁻¹³ based on distributed approximating functionals (DAF), has been introduced as a means of representing any derivative operator accurately. It has been used to obtain suitable coordinate representations for both the kinetic energy operator and the free-propagator. Because a DAF is not a standard basis set expansion, it is not a projector onto an invariant subspace; it is an approach in which every grid point plays the role of an origin associated with its own (local and possibly different) basis.¹³ In many ways, DAFs bear similarities to the “wavelet” approach for solving problems in digital signal processing¹⁴ and computational fluid mechanics.¹⁵ (Some of the connections among wavelets, delta sequences and DAFs are discussed in Ref. 16.)

A DAF approximation to a function (or its derivatives) can be obtained from a variational minimization procedure¹³ using a moving-least-squares type of method. The most studied DAF, the Hermite-DAF, can be derived in this fashion (although it was initially derived by other methods as a means to represent the action of the free propagator,⁸) and has been used to solve a variety of problems in quantum dynamics^{10,17-27} and various nonlinear partial differential equations²⁸⁻³¹ accurately. Several new forms of DAFs have

been derived and used for various quantum mechanical problems.³²⁻³⁵

In this paper we consider the application of a DAF on functions having particular symmetry, to obtain their (appropriately symmetric) derivatives. The resulting Symmetry-Adapted DAF (SADAF) can then be used to produce a matrix representation for *any* derivative operator to obtain accurate derivatives of all DAF-class functions having the prescribed symmetry. Here, we use SADAFs to construct a coordinate representation for the triatomic Adiabatically Adjusting Principal Axis Hyperspherical (APH) coordinate system Hamiltonian.^{36,37} The accuracy of this SADAF approach is later tested by obtaining some ($J=0$) ro-vibrational states for the H_3^+ molecular ion by iterative diagonalization of the SADAF represented APH Hamiltonian matrix using the Arnoldi procedure.

One could, of course, propose to treat the ro-vibrational states problem without using any symmetry. However, a careful examination of symmetry considerations leads to a significant computational simplification. For the case of three identical atoms, there is permutation symmetry which implies that interchanging any two atoms does not alter the potential energy. The six possible permutation operations belong to the permutation group S_3 . Further, any two conformations that are mirror images must have the same potential energy. The potential energy surface for three identical atoms then must have 12-fold symmetry and a full utilization of this symmetry requires storage of the wavefunctions on only 1/12-th of the grid points. This reduces the storage requirements for the associated matrices. In the case of two identical atoms, two permutation operations, belonging to the permutation group S_2 , and one reflection exist. Accounting for these symmetries leads to enormous simplifications and

^{a)}Electronic mail: kouri@uh.edu

significantly more robust computational algorithms. The computational savings, for heavier systems, could be even more (than for lighter systems like H_3^+) due to the smaller de Broglie wavelength. For example, for triatomic oxygen (ozone) the small de Broglie wavelength would require a matrix of size in excess of a million by million to be stored. Clearly, this is not practical, and even if one were to be able to store a matrix of that size, the slow N^3 scaling of existing algorithms employed by the commonly used eigenvalue solvers would require an impractically long computation time. Thus, some consideration of symmetry is a practical necessity.

This paper is organized as follows. In Sec. II we derive the Symmetry-Adapted Distributed Approximating Functionals (SADAFs) acting on one-dimensional functions with symmetry. The reason for treating one-dimensional functions will be clear in Sec. III, where we represent the rovibrational triatomic Hamiltonian in the APH coordinate system, using the SADAF representation derived in Sec. II. This representation is then tested in Secs. IV and V, first without considering any potential and then using the well-studied H_3^+ molecular ion potential energy surface due to Meyer, Botschwina and Burton (MBB).³⁸ In Sec. VI we present our conclusions.

II. SYMMETRY-ADAPTED DISTRIBUTED APPROXIMATING FUNCTIONALS (SADAFS)

The DAF approximation to the k -th derivative of a function can be expressed as

$$f_{DAF}^{(k)}(x) = \int_{-\infty}^{\infty} \delta_{DAF}^{(k)}(x-x') f(x') dx', \quad (1)$$

where the accuracy is governed by the Fourier-space characteristics of the DAF window.⁸⁻¹³ One may approximate the integral over x' by an appropriate sampling to obtain a simple and accurate⁸⁻¹³ way to calculate the value of a function and its k -th derivative, at any point on or off a grid chosen for discretization, as a matrix-vector product. We shall employ the Hermite-DAF,⁸⁻¹³

$$\begin{aligned} \delta_{DAF}^{(k)}(x-x') &\equiv \delta_{\sigma, M}^{(k)}(x-x') \\ &= \frac{1}{\sigma \sqrt{2\pi}} \left(\frac{-1}{\sqrt{2\sigma}} \right)^k \exp\left(-\frac{(x-x')^2}{2\sigma^2} \right) \\ &\quad \times \sum_{n=0}^{M/2} \left(-\frac{1}{4} \right)^n \frac{1}{n!} H_{2n+k} \left(\frac{x-x'}{\sqrt{2\sigma}} \right), \end{aligned} \quad (2)$$

where H_j is the j -th Hermite polynomial. (Note that due to the Gaussian, a discretized DAF matrix will be highly banded.) As discussed in Ref. 13, the accuracy of the calculation, when this expression for the DAF (along with an appropriate discretization scheme) is used in Eq. (1), can be made arbitrarily high for any point on or off the chosen grid of discretization by choosing appropriate values of the Hermite-DAF parameters M and σ/Δ . [Here, Δ is the grid spacing when Eq. (1) is approximated by a quadrature on a uniform grid.] When the M and σ/Δ are optimized, the re-

sulting approximation becomes insensitive to the specific choice of grid points. This feature is the so-called ‘‘well-tempered’’ nature of the DAF.^{8,13}

If the function, $f(x)$, is a periodic function of x scaled to the interval $[0, 2\pi]$, i.e., $f(x \pm 2m\pi) = f(x)$ for all integral values of m , Eq. (1) simplifies to

$$f_{DAF}^{(k)}(x) = \int_0^{2\pi} D_{DAF}^{(k)}(x-x') f(x') dx', \quad (3)$$

where $D_{DAF}^{(k)}(x-x') = \sum_{n=-\infty}^{\infty} \delta_{DAF}^{(k)}(x-x'+2n\pi)$. Although, for the sake of formal correctness, we have taken the limits of the preceding sum to be infinite, the banded nature of $\delta_{DAF}^{(k)}(x-x')$ assures that the DAF is significantly nonzero only in a finite neighborhood of x . Hence, the upper and lower limits of the sum can be taken, in fact, to be finite and small. The actual values chosen, however, depend on the choice of σ/Δ and M (for the Hermite-DAF), and the number of grid points, N (to be discussed below). Hence, $D_{DAF}^{(k)}(x-x') = \sum_{n=-n_0}^{n_0} \delta_{DAF}^{(k)}(x-x'+2n\pi)$ is a numerically accurate definition. Although one is free to approximate the integral in Eq. (3) by using any quadrature scheme, we discuss here the result of using a simple trapezoidal-rule quadrature approximation to the integral using grid points $\{x_j\}$. This leads to

$$\begin{aligned} f_{DAF}^{(k)}(x) &= \frac{1}{2} [\Delta x D_{DAF}^{(k)}(x-x_0)] f(x_0) \\ &\quad + \sum_{j=1}^{N-1} [\Delta x D_{DAF}^{(k)}(x-x_j)] f(x_j) \\ &\quad + \frac{1}{2} [\Delta x D_{DAF}^{(k)}(x-x_N)] f(x_N), \end{aligned} \quad (4)$$

where $x_j = j \Delta x$ for a uniform grid spacing $\Delta x = 2\pi/N$ and the point x can be either on the grid or off. Since $x_N = N \Delta x = 2\pi$, $x_0 = 0$, $f(x_0) = f(0) = f(2\pi) = f(x_N)$ and $D(x-x_N) = \sum_{n=-\infty}^{\infty} \delta_{DAF}^{(k)}(x-x_N+2n\pi) = \sum_{(n-1)=-\infty}^{\infty} \delta_{DAF}^{(k)}(x-x_0+2(n-1)\pi) = D(x-x_0)$, Eq. (4) takes the form

$$f_{DAF}^{(k)}(x) = \sum_{j=1}^N [\Delta x D_{DAF}^{(k)}(x-x_j)] f(x_j). \quad (5)$$

When x is on the grid, the quantity in the square brackets above, is a circulant-Toeplitz (discrete-coordinate) matrix representation for the k -th derivative operator acting on a periodic function. This derivative operation is a discrete convolution, and hence a fast-Fourier transform can be used efficiently to carry out the calculation. In general, for an evenly spaced grid, direct calculation of Eq. (5) requires only $W \times N$ floating point multiplications and $\{2W(N-2W) + W(2W+1) - W(W-1)/2\}$ floating point additions, where W is the number of grid points over which the DAF is numerically significant. Hence, this derivative calculation has *linear scaling* for large N .

We now derive SADAF expressions for a k -th derivative operator acting on one-dimensional functions belonging to some point group, \mathbf{G} . Let $\{R\}$ denote the set of operations in this point group and let h be the total number of such opera-

tions in \mathbf{G} . Let the function, f [of Eq. (5)], transform according to the λ' -th column of the j' -th irreducible representation of \mathbf{G} , i.e., $f \equiv f_{\lambda'}^{[j']}$ is the λ' -th basis function for the j' -th irreducible representation. Consider now the scalar product, in the domain $[0, 2\pi]$, of the k -th derivative of $f_{\lambda'}^{[j']}$, i.e., $f_{\lambda'}^{[j'] (k)}$, with a function $g_{\lambda}^{[j]}$, which transforms according to the λ -th column of the j -th irreducible representation of \mathbf{G} ,

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \int_0^{2\pi} dx \int_0^{2\pi} dx' g_{\lambda}^{[j]}(x) D_{DAF}^{(k)}(x-x') f_{\lambda'}^{[j']}(x'). \quad (6)$$

The integrals in Eq. (6) are divided into h parts to obtain

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \sum_{l=0}^{(h-1)} \int_{2\pi/h l}^{2\pi/h(l+1)} dx \sum_{l'=0}^{(h-1)} \int_{2\pi/h l'}^{2\pi/h(l'+1)} dx' \times g_{\lambda}^{[j]}(x) D_{DAF}^{(k)}(x-x') f_{\lambda'}^{[j']}(x'). \quad (7)$$

Consider $R \equiv R(l) \in \mathbf{G}$, such that for all x that belong to the interval $[(2\pi/h)l, (2\pi/h)(l+1)]$, $y \equiv Rx$ belongs to the interval $[0, 2\pi/h]$. The previous equation can then be rewritten as

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \sum_{R \in \mathbf{G}} \int_{R^{-1}(0)}^{R^{-1}(2\pi/h)} C_{R^{-1}} dx \sum_{R' \in \mathbf{G}} \int_{R'^{-1}(0)}^{R'^{-1}(2\pi/h)} C_{R'^{-1}} dx' \times g_{\lambda}^{[j]}(x) D_{DAF}^{(k)}(x-x') f_{\lambda'}^{[j']}(x'), \quad (8)$$

where C_R is $+1$ if R is a rotation and -1 if R is a reflection. (Note that for a one-dimensional function inversion, reflection operations are identical; hence there are only two possible operations in the group: rotation and reflection.) If we now use $y = Rx$, which implies $R^{-1}y = x$ and $C_{R^{-1}} dy = dx$, and similar definitions for the primed variables, then

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \sum_{R \in \mathbf{G}} \int_0^{2\pi/h} dy \sum_{R' \in \mathbf{G}} \int_0^{2\pi/h} dy' g_{\lambda}^{[j]}(R^{-1}y) \times D_{DAF}^{(k)}(R^{-1}y - R'^{-1}y') f_{\lambda'}^{[j']}(R'^{-1}y'), \quad (9)$$

since $[C_{R^{-1}}]^2 = 1$, by definition. Following Wigner's notation convention,³⁹ we note that

$$f_{\lambda'}^{[j']}(R^{-1}x) = P_R f_{\lambda'}^{[j']}(x), \quad (10)$$

where the set $\{P_R\}$ is isomorphic to the set $\{R\}$, but acts on functions rather than coordinates. Using this result in Eq. (9), we obtain

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \int_0^{2\pi/h} dy \int_0^{2\pi/h} dy' g_{\lambda}^{[j]}(y) \times \left[\sum_{R \in \mathbf{G}} \sum_{R' \in \mathbf{G}} P_R^{\dagger} D_{DAF}^{(k)}(R^{-1}y - R'^{-1}y') P_{R'} \right] f_{\lambda'}^{[j']}(y), \quad (11)$$

for a real function, $g_{\lambda}^{[j]}$. From the well-known relations,³⁹

$$P_R g_{\lambda}^{[j]}(x) = \sum_{\kappa=1}^{l_j} g_{\kappa}^{[j]}(x) \Gamma_{\kappa\lambda}^{(j)}(R) \quad (12)$$

and

$$P_R f_{\lambda'}^{[j']}(x) = \sum_{\kappa'=1}^{l_{j'}} f_{\kappa'}^{[j']}(x) \Gamma_{\kappa'\lambda'}^{(j')}(R), \quad (13)$$

where l_j is the dimension of the j -th irreducible representation (and $\sum_j l_j^2 = h$, the total number of operations in the group) and $\Gamma_{\kappa\lambda}^{(j)}(R)$ is the (κ, λ) -th element in the representation matrix of R in the j -th irreducible representation, Eq. (11) can be rewritten as

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \int_0^{2\pi/h} dy \int_0^{2\pi/h} dy' \sum_{\kappa=1}^{l_j} \sum_{\kappa'=1}^{l_{j'}} g_{\kappa}^{[j]}(y) \times \left[\sum_{R \in \mathbf{G}} \sum_{R' \in \mathbf{G}} \Gamma_{\kappa\lambda}^{(j)*}(R) D_{DAF}^{(k)}(R^{-1}y - R'^{-1}y') \times \Gamma_{\kappa'\lambda'}^{(j')}(R') \right] f_{\kappa'}^{[j']}(y'). \quad (14)$$

Now, if the functions $f_{\kappa'}^{[j']}$ and $g_{\kappa}^{[j]}$ are normalized in the interval $[0, 2\pi]$, then using Eqs. (12), (13) and the "Great Orthogonality Theorem,"⁴⁰ we may define functions $\tilde{f}_{\kappa'}^{[j']}$ $\equiv \sqrt{h/l_{j'}} f_{\kappa'}^{[j']}$ and $\tilde{g}_{\kappa}^{[j]} \equiv \sqrt{h/l_j} g_{\kappa}^{[j]}$ that are normalized according to

$$\sum_{\kappa'=1}^{l_{j'}} \int_0^{2\pi/h} dy |\tilde{f}_{\kappa'}^{[j']}(y)|^2 = 1, \quad (15)$$

and

$$\sum_{\kappa=1}^{l_j} \int_0^{2\pi/h} dy |\tilde{g}_{\kappa}^{[j]}(y)|^2 = 1. \quad (16)$$

Using these in Eq. (14), one obtains

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \int_0^{2\pi/h} dy \int_0^{2\pi/h} dy' \sum_{\kappa=1}^{l_j} \sum_{\kappa'=1}^{l_{j'}} \tilde{g}_{\kappa}^{[j]}(y) \times \left\{ \sqrt{\frac{l_j}{h}} \sum_{R \in G} \sum_{R' \in G} \Gamma_{\kappa\lambda}^{(j)*}(R) \times D_{DAF}^{(k)}(R^{-1}y - R'^{-1}y') \Gamma_{\kappa'\lambda'}^{(j')}(R') \sqrt{\frac{l_{j'}}{h}} \tilde{f}_{\kappa'}^{[j']}(y') \right\} \quad (17)$$

The quantities inside the curly brackets above represent the SADAF operator acting on (appropriately normalized) functions with the relevant symmetry. Although, in principle, any quadrature scheme (e.g., Monte Carlo,⁴¹ quadrature on any uneven grid, etc.) can be used to approximate the integrals in Eq. (17), the results from a discrete representation of the integrals using an extended trapezoidal rule⁴¹ are presented here. This leads to a matrix (coordinate) representation for the SADAF k -th derivative operator,

$$\int_0^{2\pi} dx g_{\lambda}^{[j]}(x) f_{\lambda'}^{[j'] (k)}(x) = \Delta y \sum_{i=0}^L \sum_{l=0}^L \sum_{\kappa=1}^{l_j} \sum_{\kappa'=1}^{l_{j'}} \tilde{g}_{\kappa}^{[j]}(y_i) \times \left[\Delta y \sqrt{\frac{l_j}{h}} \frac{1}{2} (2 - \delta_{y_i,0} - \delta_{y_i, 2\pi/h}) \times \sum_{R \in G} \sum_{R' \in G} \Gamma_{\kappa\lambda}^{(j)*}(R) D_{DAF}^{(k)}(R^{-1}y_i - R'^{-1}y_l) \Gamma_{\kappa'\lambda'}^{(j')}(R') \times \frac{1}{2} (2 - \delta_{y_l,0} - \delta_{y_l, \frac{2\pi}{h}}) \sqrt{\frac{l_{j'}}{h}} \tilde{f}_{\kappa'}^{[j']}(y_l) \right] = \Delta y \sum_{i=0}^L \sum_{l=0}^L \sum_{\kappa=1}^{l_j} \sum_{\kappa'=1}^{l_{j'}} \ddot{g}_{\kappa}^{[j]}(y_i) \times \left\{ \Delta y \sqrt{\frac{l_j (2 - \delta_{y_i,0} - \delta_{y_i, \frac{2\pi}{h}})}{2h}} \times \sum_{R \in G} \sum_{R' \in G} \Gamma_{\kappa\lambda}^{(j)*}(R) D_{DAF}^{(k)}(R^{-1}y_i - R'^{-1}y_l) \Gamma_{\kappa'\lambda'}^{(j')}(R') \times \sqrt{\frac{l_{j'} (2 - \delta_{y_l,0} - \delta_{y_l, \frac{2\pi}{h}})}{2h}} \right\} \tilde{f}_{\kappa'}^{[j']}(y_l), \quad (18)$$

where $L = 2\pi/(h \Delta y)$ and $y_i = i \Delta y$, and we have defined new discrete functions,

$$\tilde{f}_{\kappa'}^{[j']}(y_j) \equiv \frac{1}{\sqrt{2}} \sqrt{2 - \delta_{y_j,0} - \delta_{y_j, \frac{2\pi}{h}}} \tilde{f}_{\kappa'}^{[j']}(y_j) \quad (19)$$

and

$$\ddot{g}_{\kappa}^{[j]}(y_i) \equiv \frac{1}{\sqrt{2}} \sqrt{2 - \delta_{y_i,0} - \delta_{y_i, 2\pi/h}} \tilde{g}_{\kappa}^{[j]}(y_i), \quad (20)$$

that obey the normalization condition from the Trapezoidal rule approximation to Eqs. (15) and (16).

Since terms inside the curly brackets ($\{ \}$) in Eq. (18) constitute the matrix (coordinate) representation for the SADAF k -th derivative operator acting on functions with the aforementioned symmetry, it is clear that the representation matrix $\Gamma^{(j)}(R)$ is used as a similarity transformation on the DAF, which results in the projection of the k -th derivative of functions that transform according to the λ' -th column of the j' -th irreducible representation.

Further, “even” derivative operators preserve the symmetry of the functions they act on. Hence, for a nonzero result it is required that the functions $f_{\lambda'}^{[j']}$ and $g_{\lambda}^{[j]}$ have the same symmetry and thus $\lambda = \lambda'$ and $j = j'$ for even derivative operations. Odd derivative operators change the symmetry, under reflection, of the functions to which they are applied. Hence, in this case, (λ, j) and (λ', j') are different and $f_{\lambda'}^{[j']}$ and $g_{\lambda}^{[j]}$ belong to different irreducible representations (or different columns of the same irreducible representation), with the symmetry of one being related to the other by a change in reflection parity.

Alternate ways to arrive at the SADAF representation for the k -th derivative operator include the construction of the projection operators,³⁹

$$\mathcal{P}_{\kappa\kappa}^{(j)} = \frac{l_j}{h} \sum_R \Gamma_{\kappa\kappa}^{(j)}(R) * P_R, \quad (21)$$

or

$$\mathcal{P}^{(j)} = \frac{l_j}{h} \sum_R \chi^{(j)}(R) * P_R, \quad (22)$$

followed by their use in the similarity transformation of the periodic symmetry discrete DAF expression in Eq. (5). The $\chi^{(j)}(R)$ (the “characters”) are the sums (the traces) of the diagonal elements, $\Gamma_{\kappa\kappa}^{(j)}(R)$, for the j -th irreducible representation.

As usual, if the eigenfunctions of such derivative matrices are calculated, one obtains eigenfunctions that transform according to the λ' -th column of the j' -th irreducible representation, namely, $\psi_{\lambda'}^{[j']}(x)$. (Of course, in quantum mechanical applications, the choice of the point group is determined by the symmetry of the potential, since the kinetic energy operator is invariant to all symmetry operations belonging to

the rotation group.) To obtain the other functions in the j' -th irreducible representation, we make use of the transfer operator,³⁹

$$\mathcal{P}_{\lambda\lambda'}^{(j')} = \frac{l_{j'}}{\hbar} \sum_R \Gamma_{\lambda\lambda'}^{(j')}(R) * P_R, \quad (23)$$

so that

$$\mathcal{P}_{\lambda\lambda'}^{(j')} \psi_{\lambda'}^{[j']1}(x) = \psi_{\lambda}^{[j']1}(x) \delta_{\lambda'\lambda}. \quad (24)$$

Clearly, the eigenvalues for all $\{\psi_{\lambda}^{[j']1}(x)\}$ (for $\lambda = 1, \dots, l_{j'}$) are the same.

III. THE ADIABATICALLY ADJUSTING PRINCIPAL AXIS HYPERSPHERICAL COORDINATES (APH) – SADAF REPRESENTATION

The body-fixed, mass-scaled Jacobi coordinates^{42,43} are inappropriate for treating the strong-interaction region in triatomic systems having D_{3h} point group symmetry (i.e., triatomic molecules where all three atoms are the same) because the application of an element of this point group to a single Jacobi coordinate results in mixing of the other coordinates.⁴⁴ Hyperspherical coordinates resolve this problem. The APH coordinate system,^{36,37} in particular, results in a very simple expression for the action of the elements in the point group, since only one of the variables (the azimuthal angle) is affected by this action. Furthermore, the azimuthal angle in the APH system is half the azimuthal angle in the hyperspherical coordinates introduced by Smith and Whitten,⁴⁵ Johnson,^{46,47} Mead⁴⁸ and Zickendraht,⁴⁹ which helps avoid half-integer angular momenta, which are characteristic of these other hyperspherical coordinates^{46,47,45,49} and whose occurrence is a manifestation of the ‘‘Berry’’ phase.⁵⁰ As a result of this, a system of three similar atoms has a C_{6v} point group symmetry in APH coordinates (which is isomorphic to D_{3h}), as discussed in Ref. 37. The only variable affected by the symmetry is the azimuthal angle, χ , about the C_6 -axis. In this Section we first rewrite the APH kinetic energy operator in a form that is convenient for our purpose; following this, a SADAF representation is constructed.

Consider the kinetic energy part of the triatom Hamiltonian in APH coordinates,^{36,37,46,47}

$$\begin{aligned} T = & -\frac{\hbar^2}{2\mu\rho^5} \frac{\partial}{\partial\rho} \rho^5 \frac{\partial}{\partial\rho} - \frac{\hbar^2}{2\mu\rho^2} \left[\frac{4}{\sin 2\theta} \frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} \right. \\ & \left. + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\chi^2} \right] + \frac{\hat{J}_x^2}{\mu\rho^2(1+\sin\theta)} + \frac{\hat{J}_y^2}{2\mu\rho^2\sin^2\theta} \\ & + \frac{\hat{J}_z^2}{\mu\rho^2(1-\sin\theta)} - \frac{i\hbar\cos\theta}{\mu\rho^2\sin^2\theta} \hat{J}_y \frac{\partial}{\partial\chi}. \end{aligned} \quad (25)$$

The eigenfunctions of this kinetic energy operator are proportional to $\rho^{-5/2}$,³⁷ and hence are not well behaved at $\rho = 0$. To obtain well-behaved solutions, Pack and Parker³⁷ introduced an operator, $\tilde{T} = \rho^{5/2} T \rho^{-5/2}$, a transform of T , by

$$\begin{aligned} \tilde{T} = & \rho^{5/2} T \rho^{-5/2} \\ = & -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial\rho^2} + \frac{15\hbar^2}{8\mu\rho^2} - \frac{\hbar^2}{2\mu\rho^2} \left[\frac{4}{\sin 2\theta} \frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} \right. \\ & \left. + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\chi^2} \right] + \frac{A_\theta + B_\theta}{2\mu\rho^2} \hat{J}^2 + \frac{1}{\mu\rho^2} \left[C_\theta - \frac{A_\theta + B_\theta}{2} \right] \hat{J}_z^2 \\ & + \left(\frac{A_\theta - B_\theta}{2\mu\rho^2} \right) \frac{1}{2} [\hat{J}_+^2 + \hat{J}_-^2] - \frac{\hbar}{2\mu\rho^2} \\ & \times \left(\frac{\cos\theta}{\sin^2\theta} \frac{\partial}{\partial\chi} \right) [\hat{J}_- - \hat{J}_+]. \end{aligned} \quad (26)$$

Here $A_\theta = 1/(1+\sin\theta)$, $B_\theta = 1/2\sin^2\theta$ and $C_\theta = 1/(1-\sin\theta)$ are related to the moments of inertia of the triatom in the body-fixed coordinates, \hat{J}_x , \hat{J}_y and \hat{J}_z are components of \hat{J} , the total angular momentum of the three-atom system, $\hat{J}_\pm = \hat{J}_x \mp i\hat{J}_y$ and $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$. We form the matrix element

$$\begin{aligned} \langle \mathcal{D}_{\Lambda M}^{J_p} | \tilde{T} | \mathcal{D}_{\Lambda' M'}^{J_p} \rangle = & \delta_{\Lambda, \Lambda'} \left\{ -\frac{\hbar}{2\mu} \left\{ \frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho^2} \left[\frac{4}{\sin 2\theta} \frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\chi^2} \right] \right\} \right\} \\ & + \delta_{\Lambda, \Lambda'} \left\{ \frac{A_\theta + B_\theta}{2\mu\rho^2} \hbar^2 J(J+1) + \frac{15\hbar^2}{8\mu\rho^2} + \frac{1}{\mu\rho^2} \left[C_\theta - \frac{A_\theta + B_\theta}{2} \right] \hbar^2 \Lambda^2 \right\} \\ & + \delta_{\Lambda+1, \Lambda'} \left\{ -\frac{\hbar}{2\mu\rho^2} f(\Lambda, J, p) \left(\frac{\cos\theta}{\sin^2\theta} \frac{\partial}{\partial\chi} \right) \right\} + \delta_{\Lambda+2, \Lambda'} \left\{ g(\Lambda, J, p) \frac{A_\theta - B_\theta}{4\mu\rho^2} \right\} \\ & + \delta_{\Lambda-1, \Lambda'} \left\{ -\frac{\hbar}{2\mu\rho^2} f(\Lambda, J, p) \left(\frac{\cos\theta}{\sin^2\theta} \frac{\partial}{\partial\chi} \right) \right\} + \delta_{\Lambda-2, \Lambda'} \left\{ g(\Lambda, J, p) \frac{A_\theta - B_\theta}{4\mu\rho^2} \right\}, \end{aligned} \quad (27)$$

TABLE I. Irreducible representations of E_1 in the point group C_{6v} . Basis $[x, y]$.

	E	C_6	C_6^{-1}	C_3	C_3^{-1}	C_2
x'	x	$\frac{1}{2}x - \frac{\sqrt{3}}{2}y$	$\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$-\frac{1}{2}x - \frac{\sqrt{3}}{2}y$	$-\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$-x$
y'	y	$\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$-\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$\frac{\sqrt{3}}{2}x - \frac{1}{2}y$	$-\frac{\sqrt{3}}{2}x - \frac{1}{2}y$	$-y$
	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$
	σ_{v_1}	σ_{v_2}	σ_{v_3}	σ_{d_1}	σ_{d_2}	σ_{d_3}
x'	x	$-\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$-\frac{1}{2}x - \frac{\sqrt{3}}{2}y$	$\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$-x$	$\frac{1}{2}x - \frac{\sqrt{3}}{2}y$
y'	$-y$	$\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$-\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$\frac{\sqrt{3}}{2}x - \frac{1}{2}y$	y	$-\frac{\sqrt{3}}{2}x - \frac{1}{2}y$
	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$

where $\mathcal{D}_{\Lambda M}^{Jp}$ are the normalized Wigner \mathcal{D} functions⁵¹ with definite parity, p , defined in³⁷

$$\mathcal{D}_{\Lambda M}^{Jp} = \sqrt{\frac{2J+1}{16\pi^2(1+\delta_{\Lambda 0})}} \times [\mathcal{D}_{\Lambda M}^J + (-1)^{J+\Lambda+p} \mathcal{D}_{-\Lambda M}^J]. \quad (28)$$

The $f(\Lambda, J, p)$ are the Coriolis coupling coefficients and are defined by³⁷

$$f(\Lambda, J, p) = \langle \mathcal{D}_{\Lambda M}^{Jp} | (\hat{J}_- - \hat{J}_+) | \mathcal{D}_{\Lambda' M'}^{Jp} \rangle, \quad (29)$$

and the $g(\Lambda, J, p)$ are the asymmetric top coupling coefficients defined by³⁷

$$g(\Lambda, J, p) = \langle \mathcal{D}_{\Lambda M}^{Jp} | (\hat{J}_+^2 + \hat{J}_-^2) | \mathcal{D}_{\Lambda' M'}^{Jp} \rangle. \quad (30)$$

In the coordinate representation, the Hamiltonian in Eq. (27) can be written in terms of the tensor products,

$$\begin{aligned} \tilde{T}_{\Lambda, \Lambda} = & \left[T_\rho + \frac{15\hbar^2}{8\mu\rho^2} I_\rho \right] \otimes I_\theta \otimes I_\chi + \left[\frac{-\hbar^2}{2\mu\rho^2} I_\rho \right] \otimes T_\theta \otimes I_\chi \\ & + \left[\frac{-\hbar^2}{2\mu\rho^2} I_\rho \right] \otimes 2B_\theta \otimes T_\chi + \left[J(J+1) \frac{\hbar^2}{2\mu\rho^2} I_\rho \right] \\ & \otimes [A_\theta + B_\theta] \otimes I_\chi + \left[\Lambda^2 \frac{\hbar^2}{2\mu\rho^2} I_\rho \right] \\ & \otimes [2C_\theta - A_\theta - B_\theta] \otimes I_\chi, \end{aligned} \quad (31)$$

$$\tilde{T}_{\Lambda, \Lambda \pm 1} = \left[\frac{-\hbar^2}{2\mu\rho^2} f(\Lambda, J, p) I_\rho \right] \otimes D_\theta \otimes T_\chi^1 \quad (32)$$

and

$$\tilde{T}_{\Lambda, \Lambda \pm 2} = \left[\frac{-\hbar^2}{2\mu\rho^2} g(\Lambda, J, p) I_\rho \right] \otimes \frac{1}{2} [A_\theta - B_\theta] \otimes I_\chi, \quad (33)$$

where the symbol \otimes implies a direct product, $D_\theta = \cos\theta/\sin^2\theta$ is a diagonal matrix in θ , I_ρ , I_θ and I_χ are unit matrices in ρ , θ and χ respectively, T_ρ is the matrix coordinate representation of the operator $(-\hbar/2\mu)(\partial^2/\partial\rho^2)$, T_θ is the matrix coordinate representation of the operator $(-4/\sin 2\theta)(\partial/\partial\theta)\sin 2\theta(\partial/\partial\theta)$, T_χ is the matrix coordinate representation of the operator $(-\partial^2/\partial\chi^2)$, T_χ^1 is the matrix representation of the operator $\partial/\partial\chi$ and A_θ , B_θ and C_θ are diagonal matrices in θ as defined above.

In the next subsections we obtain the SADAF-representation for the operators T_ρ , T_θ , T_χ and T_χ^1 , which then can be used to form the total Hamiltonian matrix.

A. Azimuthal angle matrices T_χ and T_χ^1

We consider all the possibilities for the three atom case, namely, (i) all atoms are dissimilar—the ABC case, (ii) two atoms are similar—the A_2B case; and (iii) all three atoms are similar—the A_3 case.

In the case of three dissimilar atoms, the potential energy surface has a C_1 point group symmetry along the body-fixed y -axis in the APH coordinate system. Hence, χ , the azi-

TABLE II. Irreducible representations of E_2 in the point group C_{6v} . Basis $[(x^2-y^2), 2xy]$.

	E	C_6	C_6^{-1}	C_3	C_3^{-1}	C_2
$x'^2-y'^2$	x^2-y^2	$-\frac{1}{2}(x^2-y^2)$ $-\frac{\sqrt{3}}{2}2xy$	$-\frac{1}{2}(x^2-y^2)$ $+\frac{\sqrt{3}}{2}2xy$	$-\frac{1}{2}(x^2-y^2)$ $+\frac{\sqrt{3}}{2}2xy$	$-\frac{1}{2}(x^2-y^2)$ $-\frac{\sqrt{3}}{2}2xy$	x^2-y^2
$2x'y'$	$2xy$	$\frac{\sqrt{3}}{2}(x^2-y^2)$ $-\frac{1}{2}2xy$	$-\frac{\sqrt{3}}{2}(x^2-y^2)$ $-\frac{1}{2}2xy$	$-\frac{\sqrt{3}}{2}(x^2-y^2)$ $-\frac{1}{2}2xy$	$\frac{\sqrt{3}}{2}(x^2-y^2)$ $-\frac{1}{2}2xy$	$2xy$
	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
	σ_{v_1}	σ_{v_2}	σ_{v_3}	σ_{d_1}	σ_{d_2}	σ_{d_3}
$x'^2-y'^2$	x^2-y^2	$-\frac{1}{2}(x^2-y^2)$ $-\frac{\sqrt{3}}{2}2xy$	$-\frac{1}{2}(x^2-y^2)$ $+\frac{\sqrt{3}}{2}2xy$	$-\frac{1}{2}(x^2-y^2)$ $+\frac{\sqrt{3}}{2}2xy$	x^2-y^2	$-\frac{1}{2}(x^2-y^2)$ $-\frac{\sqrt{3}}{2}2xy$
$2x'y'$	$-2xy$	$-\frac{\sqrt{3}}{2}(x^2-y^2)$ $\frac{1}{2}2xy$	$\frac{\sqrt{3}}{2}(x^2-y^2)$ $\frac{1}{2}2xy$	$\frac{\sqrt{3}}{2}(x^2-y^2)$ $\frac{1}{2}2xy$	$-2xy$	$-\frac{\sqrt{3}}{2}(x^2-y^2)$ $\frac{1}{2}2xy$
	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$

muthal angle, ranges from 0 to 2π , and the only symmetry here is the periodicity of functions of χ (with period 2π). From Eq. (5),

$$T_\chi(\chi_i, \chi_j) = -\Delta\chi D_{DAF}^{(2)}(\chi_i - \chi_j) \tag{34}$$

and

$$T_\chi^1(\chi_i, \chi_j) = \Delta\chi D_{DAF}^{(1)}(\chi_i - \chi_j), \tag{35}$$

both expressions leading to circulant-Toeplitz matrices.

In the case of two similar atoms, the potential surface has a C_{2v} point group symmetry along the body fixed y -axis, leading to four different one-dimensional irreducible representations, namely, A_1 , A_2 , B_1 and B_2 . The characters for these irreducible representations are $\{1, (-1)^p, (-1)^q, (-1)^{(p+q)}\}$, where p and q represent the rotation symmetry (under C_2) and reflection symmetry [under $\sigma_v(yz)$], respectively, and $(p+q)$ represents the symmetry under reflection

through the plane $\sigma_{v'}(xy)$. Using these characters in Eq. (18), we obtain

$$\begin{aligned} T_\chi(\chi_i, \chi_j) &= \Delta\chi \frac{\sqrt{2 - \delta_{\chi_i, 0} - \delta_{\chi_i, \pi/2}}}{\sqrt{2}} [D_{DAF}^{(2)}(\chi_i - \chi_j) + (-1)^p \\ &\quad \times D_{DAF}^{(2)}(\chi_i - \chi_j - \pi) + (-1)^q D_{DAF}^{(2)}(\chi_i + \chi_j) \\ &\quad + (-1)^{(p+q)} D_{DAF}^{(2)}(\chi_i + \chi_j - \pi)] \frac{\sqrt{2 - \delta_{\chi_j, 0} - \delta_{\chi_j, \pi/2}}}{\sqrt{2}} \end{aligned} \tag{36}$$

and

$$\begin{aligned} T_\chi^1(\chi_i, \chi_j) &= \Delta\chi \frac{\sqrt{2 - \delta_{\chi_i, 0} - \delta_{\chi_i, \pi/2}}}{\sqrt{2}} [D_{DAF}^{(1)}(\chi_i - \chi_j) + (-1)^p \\ &\quad \times D_{DAF}^{(1)}(\chi_i - \chi_j - \pi) + (-1)^q D_{DAF}^{(1)}(\chi_i + \chi_j) \\ &\quad + (-1)^{(p+q)} D_{DAF}^{(1)}(\chi_i + \chi_j \\ &\quad - \pi)] \frac{\sqrt{2 - \delta_{\chi_j, 0} - \delta_{\chi_j, \pi/2}}}{\sqrt{2}}, \end{aligned} \tag{37}$$

where we have used the fact that $j=j'$ for the even derivatives, while for odd derivatives they are related by $(-1)^p = (-1)^{p'}$ and $(-1)^q = -(-1)^{q'}$.

For three similar atoms, i.e., A_3 , the potential surface has a C_{6v} point group symmetry along the body fixed y -axis. The one-dimensional irreducible representations in this point group are A_1, A_2, B_1, B_2 [having characters $\{1, (-1)^\alpha, 1, (-1)^\beta, (-1)^{(\alpha+\beta)}\}$ where α represents the symmetry under the rotation operations C_6, C_6^{-1} and C_2 ; β represents the

symmetry under reflections through vertical planes $\sigma_{v_1}, \sigma_{v_2}$ and σ_{v_3} ; and $(\alpha + \beta)$ represents the symmetry under reflections through dihedral planes $\sigma_{d_1}, \sigma_{d_2}$ and σ_{d_3}] and the two-dimensional irreducible representations are E_1 and E_2 (the irreducible representation matrices for which can be found in Tables I and II). Using the characters for the one-dimensional irreducible representations in Eq. (18), the derivative matrices are obtained as

$$\begin{aligned}
 T_\chi(\chi_i, \chi_j) = \Delta\chi \frac{\sqrt{2 - \delta_{\chi_i, 0} - \delta_{\chi_i, \pi/6}}}{\sqrt{2}} & \left[D_{DAF}^{(2)}(\chi_i - \chi_j) + (-1)^\alpha D_{DAF}^{(2)}\left(\chi_i - \chi_j - \frac{\pi}{3}\right) + (-1)^\alpha D_{DAF}^{(2)}\left(\chi_i - \chi_j + \frac{\pi}{3}\right) \right. \\
 & + D_{DAF}^{(2)}\left(\chi_i - \chi_j - \frac{2\pi}{3}\right) + D_{DAF}^{(2)}\left(\chi_i - \chi_j + \frac{2\pi}{3}\right) + (-1)^\alpha D_{DAF}^{(2)}(\chi_i - \chi_j - \pi) + (-1)^\beta D_{DAF}^{(2)}(\chi_i + \chi_j) \\
 & + (-1)^\beta D_{DAF}^{(2)}\left(\chi_i + \chi_j - \frac{2\pi}{3}\right) + (-1)^\beta D_{DAF}^{(2)}\left(\chi_i + \chi_j + \frac{2\pi}{3}\right) + (-1)^{(\alpha+\beta)} D_{DAF}^{(2)}\left(\chi_i + \chi_j - \frac{\pi}{3}\right) \\
 & \left. + (-1)^{(\alpha+\beta)} D_{DAF}^{(2)}(\chi_i + \chi_j - \pi) + (-1)^{(\alpha+\beta)} D_{DAF}^{(2)}\left(\chi_i + \chi_j + \frac{\pi}{3}\right) \right] \frac{\sqrt{2 - \delta_{\chi_j, 0} - \delta_{\chi_j, \pi/2}}}{\sqrt{2}} \quad (38)
 \end{aligned}$$

and

$$\begin{aligned}
 T_\chi^1(\chi_i, \chi_j) = \Delta\chi \frac{\sqrt{2 - \delta_{\chi_i, 0} - \delta_{\chi_i, \pi/6}}}{\sqrt{2}} & \left[D_{DAF}^{(1)}(\chi_i - \chi_j) + (-1)^\alpha D_{DAF}^{(1)}\left(\chi_i - \chi_j - \frac{\pi}{3}\right) + (-1)^\alpha D_{DAF}^{(1)}\left(\chi_i - \chi_j + \frac{\pi}{3}\right) \right. \\
 & + D_{DAF}^{(1)}\left(\chi_i - \chi_j - \frac{2\pi}{3}\right) + D_{DAF}^{(1)}\left(\chi_i - \chi_j + \frac{2\pi}{3}\right) + (-1)^\alpha D_{DAF}^{(1)}(\chi_i - \chi_j - \pi) + (-1)^\beta D_{DAF}^{(1)}(\chi_i + \chi_j) \\
 & + (-1)^\beta D_{DAF}^{(1)}\left(\chi_i + \chi_j - \frac{2\pi}{3}\right) + (-1)^\beta D_{DAF}^{(1)}\left(\chi_i + \chi_j + \frac{2\pi}{3}\right) + (-1)^{(\alpha+\beta)} D_{DAF}^{(1)}\left(\chi_i + \chi_j - \frac{\pi}{3}\right) \\
 & \left. + (-1)^{(\alpha+\beta)} D_{DAF}^{(1)}(\chi_i + \chi_j - \pi) + (-1)^{(\alpha+\beta)} D_{DAF}^{(1)}\left(\chi_i + \chi_j + \frac{\pi}{3}\right) \right] \frac{\sqrt{2 - \delta_{\chi_j, 0} - \delta_{\chi_j, \pi/2}}}{\sqrt{2}}, \quad (39)
 \end{aligned}$$

where, again, we use $j=j'$ for the even derivatives, and $(-1)^\alpha = (-1)^{\alpha'}$, $(-1)^\beta = -(-1)^{\beta'}$ for odd derivatives.

In the case of the E -sets, the derivative matrices contain four blocks (each labeled by different values for κ and κ'), with the form of the (κ, κ') block being as in the term in the curly brackets in Eq. (18). (In this case, κ and κ' can assume the values 1 or 2.) We present below the form of the four blocks for the derivative matrices acting on a function which transforms according to the λ -th column of one of the E -irreducible representations. Further, to keep the expressions simple, we assume here a discretization scheme which omits the two end points, 0 and $2\pi/h$. We then have

$$\begin{aligned}
 [T_\chi]_{(\chi_i, \chi_j, \kappa, \kappa')} &= \frac{1}{6} \sum_{R \in C_{6v}} \sum_{R' \in C_{6v}} \Gamma_{\kappa\lambda}^{(j)*}(R) \\
 &\times D_{DAF}^{(2)}(R^{-1}\chi_i - R'^{-1}\chi_j) \Gamma_{\kappa'\lambda'}^{(j)}(R') \quad (40)
 \end{aligned}$$

and

$$\begin{aligned}
 [T_\chi^1]_{(\chi_i, \chi_j, \kappa, \kappa')} &= \frac{1}{6} \sum_{R \in C_{6v}} \sum_{R' \in C_{6v}} \Gamma_{\kappa\lambda}^{(j)*}(R) \\
 &\times D_{DAF}^{(1)}(R^{-1}\chi_i - R'^{-1}\chi_j) \Gamma_{\kappa'\lambda'}^{(j)}(R'). \quad (41)
 \end{aligned}$$

In these expressions, the superscript (j) can correspond to either E_1 or E_2 . For the case of the second derivative matrix, λ can take the values 1 or 2 depending on the symmetry of the function acted upon. For the first derivative, again, λ can take any of the two values for the same reason as above, but λ' must be different from λ . This is because the two columns of any E -set correspond to functions that have opposite symmetry under reflection.

B. The polar angle matrix T_θ

To obtain the SADAF representation for the $T_\theta = - (4/\sin 2\theta) (\partial/\partial\theta) \sin 2\theta (\partial/\partial\theta)$ operator, we note that the polar angle θ is defined on the domain $[0, \pi/2]$ and the eigenfunctions of the T_θ operator, the Legendre polynomials, satisfy Neumann boundary conditions (i.e., the first derivative being zero at the boundary points $\theta=0$ and $\theta=\pi/2$). Since the Legendre polynomials form a complete set, the θ dependence of any solution to the Schrödinger equation [whose kinetic energy part is described in Eq. (27)] can be expanded in terms of them, and hence also must satisfy the same boundary conditions. Furthermore, the Legendre polynomials of order l , $P_l(\cos 2\theta)$, belong to the A_1 irreducible representation of C_{2v} (which is a result of the Neumann boundary conditions and periodicity) and hence all the θ dependence of the solutions must have this symmetry. Thus, the use of C_{2v} adapted derivative operators in the formation of T_θ must result in a matrix representation that correctly acts on the Legendre polynomials. Using Eq. (37) along with the fact that $p=q=0$ for the A_1 irreducible representation,

$$\begin{aligned} \left[\frac{\partial}{\partial\theta} \right]_{\theta_i, \theta_j} &\equiv \Delta\theta \frac{\sqrt{2 - \delta_{\theta_i, 0} - \delta_{\theta_i, \pi/2}}}{\sqrt{2}} [D_{DAF}^{(1)}(\theta_i - \theta_j) \\ &+ D_{DAF}^{(1)}(\theta_i - \theta_j - \pi) + D_{DAF}^{(1)}(\theta_i + \theta_j) \\ &+ D_{DAF}^{(1)}(\theta_i + \theta_j - \pi)] \frac{\sqrt{2 - \delta_{\theta_j, 0} - \delta_{\theta_j, \pi/2}}}{\sqrt{2}}. \end{aligned} \quad (42)$$

The SADAF representation matrix for the T_θ operator can then be written as the simple matrix product,

$$(T_\theta)_{\theta_i, \theta_j} = \frac{-4}{\sin 2\theta_i} \sum_{k=1}^{N_\theta} \left[\frac{\partial}{\partial\theta} \right]_{\theta_i, \theta_k} \sin 2\theta_k \left[\frac{\partial}{\partial\theta} \right]_{\theta_k, \theta_j}, \quad (43)$$

where θ_i , θ_j and θ_k are grid points, N_θ in number.

However, the quantity $1/\sin 2\theta$, is singular at $\theta=0$ and $\theta=\pi/2$. One way to overcome this problem is to choose a grid that avoids the two singular points. To this end, the first point on the grid is chosen at $\Delta\theta/2$ and the last point at $(\pi/2 - \Delta\theta/2)$, where $\Delta\theta$ is the grid spacing. This method should work well in most cases, except when dealing with functions that exhibit rapid oscillatory behavior near the two end points 0 and $\pi/2$. In such cases, though, an alternate method could be used in view of the fact that

$$\frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} P_l(\cos 2\theta) \quad (44)$$

tends linearly to zero at $\theta=0$ and $\theta=\pi/2$. Hence, the singularity must cancel out in the limit as $\theta \rightarrow 0$ and $\theta \rightarrow \pi/2$. Therefore, the l'Hôpital rule can be used to obtain the limit of the quotient as $\theta \rightarrow 0$ and $\theta \rightarrow \pi/2$. This is done by differentiating both the numerator and denominator to obtain

$$T_\theta|_{\theta=0} = -2 \left[\frac{\partial^2}{\partial\theta^2} \sin 2\theta \frac{\partial}{\partial\theta} \right]_{\theta=0} \quad (45)$$

and

$$T_\theta|_{\theta=\pi/2} = +2 \left[\frac{\partial^2}{\partial\theta^2} \sin 2\theta \frac{\partial}{\partial\theta} \right]_{\theta=\pi/2}. \quad (46)$$

The discrete representations for these two operators can be obtained by using the SADAF representation for the derivative operators acting on functions belonging to the A_1 irreducible representation of C_{2v} ;

$$\pm 2 \sum_{k=1}^{N_\theta} \left[\frac{\partial^2}{\partial\theta^2} \right]_{\theta_i, \theta_k} \sin 2\theta_k \left[\frac{\partial}{\partial\theta} \right]_{\theta_k, \theta_j}, \quad (47)$$

where the matrix elements $[\partial^2/\partial\theta^2]_{\theta_i, \theta_k}$ and $[\partial/\partial\theta]_{\theta_k, \theta_j}$ are similar in form to the expressions, Eqs. (36) and (37).

C. The nonantihermiticity of the $\partial/\partial\theta$ and the nonhermiticity of T_θ matrices

The DAF matrix representation for the $\partial/\partial\theta$ operator in Eq. (42) is not anti-Hermitian. This makes the T_θ matrix nonHermitian. In this subsection, we will discuss the specifics of this in some detail.

From the matrix representation of $\partial/\partial\theta$ in Eq. (42), it is clear that the (θ_i, θ_j) -th element of this matrix is not the negative of its adjoint element, (θ_j, θ_i) , if the last two elements of the sum are nonzero, i.e., if $(i+j) \leq W$ or if $[(i+j) - 2(N_\theta - 1)] \leq W$, where $N_\theta = \pi/(2 \Delta\theta)$ is the number of θ -grid points, and W is the band width of the DAF, i.e., the number of grid points over which the DAF is numerically nonzero. In other words the DAF representation for $\partial/\partial\theta$ above is non-anti-Hermitian in two regions: (i) the top left triangular corner of the matrix and (ii) the bottom right triangular corner of the matrix. This makes the T_θ matrix non-Hermitian in those two regions as well. Furthermore, the size of the regions is proportional to $W \Delta\theta$.

Now, one of the properties of the DAF is that its band width is independent of the grid size $\Delta\theta$ as long as the values of σ and M are kept constant. Hence, as $\Delta\theta$ is made smaller, the total number of grid points, N_θ , increases and the ratio $W/N_\theta (= 2W \Delta\theta/\pi)$ gets smaller. Hence, as the grid spacing is reduced, so also is the region of nonhermiticity and in the continuous limit, i.e., as $\Delta\theta$ becomes infinitesimally small, this region, $W/N_\theta \propto W \Delta\theta$, becomes infinitesimally small. Hence, in the continuous limit, the T_θ matrix becomes hermitian (and the $\partial/\partial\theta$ matrix is anti-Hermitian) and we conclude that **the nonhermiticity problem is created by the finite discretization**. Furthermore, as we will see in the next section, we find that the eigenvalues of the T_θ matrix are all real, in spite of its non-Hermitian structure. Another important feature is that the T_θ matrix possesses a certain additional symmetry $[T_\theta(I, J) = T_\theta(N_\theta + 1 - I, N_\theta + 1 - J)]$ which makes it necessary to store only one half of the matrix (the upper or lower triangle), just as is the case for Hermitian matrices.

D. Radial part

In order to obtain a faithful representation for the T_ρ operator, we first examine the asymptotic behavior of the wavefunction as a function of ρ . Small ρ values (in APH coordinates) represent the situation where the three atoms are

close to each other and eventually coalesce (at $\rho=0$), while the large values of ρ represent the impending dissociation limits. Since we are interested in obtaining only rotational and vibrational states, we will concentrate on an energy range substantially lower than both of these limits. Hence, our wavefunction must decay to zero for small and large values of ρ . Where the wavefunctions become numerically insignificant will, of course, depend on the system under consideration.

We construct a domain in ρ (say $[\rho_{min}, \rho_{max}]$), and require that the wavefunction numerically tend to zero outside this region. In this case, we can discretize the region $[\rho_{min}, \rho_{max}]$, such that $\rho_i = \rho_{min} + (i-1) \times (\Delta\rho)$. Then the T_ρ operator in this domain can be written as

$$T_\rho = \Delta\rho \delta_{\sigma,M}^{(2)}(\rho_i - \rho_j), \quad (48)$$

where $\delta_{\sigma,M}^{(2)}(\rho_i - \rho_j)$ is the continuous DAF representation of the second derivative operator and has the form given in Eq. (2).

IV. COMPUTATIONAL TESTS WITH NO POTENTIAL

Testing the accuracy and the computational efficiency of the symmetry-adapted DAF expressions has been done in two stages. To begin, the potential was set to zero and the submatrices T_χ and T_θ (for all point groups for the three atom case) were independently diagonalized⁵² to obtain solutions to simple (analytically solvable) eigenvalue problems. The submatrix T_χ^1 is tested by examining its action on the eigenfunctions of T_χ . The results from these tests are discussed in this Section. In the next section, the H_3^+ molecular ion potential due to Meyer, Botschwina and Burton³⁸ is considered and ro-vibrational eigenstates calculated (using the APH-SADAF kinetic energy operator) by the Arnoldi iterative diagonalization scheme.⁵³⁻⁵⁵ The resulting eigenstates are compared with those obtained in previous studies.⁵⁶⁻⁶³ We use the Hermite-DAF given in Eq. (2), with $\sigma/\Delta = 2.5$ and $M = 60$ for all the calculations in this paper.

A. Zero-potential tests: χ -dependent operators

To test the accuracy of the SADAF representation for T_χ and T_χ^1 , consider the one-dimensional particle-in-a-ring eigenvalue problem,

$$\frac{\partial^2}{\partial\chi^2} f(\chi) = \lambda f(\chi), \quad (49)$$

with periodic boundary conditions. The eigenvalues are $\lambda = -n^2$ for integral values of n , and the periodic eigenfunctions are the corresponding Fourier functions, $\{\exp(in\chi)\}$. Direct diagonalization of the C_1 matrix representation of the second derivative operator in Eq. (34) should yield the eigenvalues λ and the eigenfunctions $f(\chi)$, the respective accuracy thus providing a measure of the efficiency of the SADAF representation. Furthermore, the C_{2v} or the C_{6v} representations for the second derivative operator can also be used; however, direct diagonalization of these matrices will yield only eigenvalues and eigenfunctions that transform according to the respective chosen irreducible representation. In Table III we outline the symmetries (i.e., the irreducible

TABLE III. Eigenvalues of the T_χ matrix and the symmetry of each eigenfunction in a specific point group.

Eigenvalue	Eigenfunction	C_1	C_{2v}	C_{6v}
0	$\cos 0x$	A	A_1	A_1
1	$\cos 1x$	A	B_1	E_1
1	$\sin 1x$	A	B_2	E_1
2	$\cos 2x$	A	A_1	E_2
2	$\sin 2x$	A	A_2	E_2
3	$\cos 3x$	A	B_1	B_1
3	$\sin 3x$	A	B_2	B_2
4	$\cos 4x$	A	A_1	E_2
4	$\sin 4x$	A	A_2	E_2
5	$\cos 5x$	A	B_1	E_1
5	$\sin 5x$	A	B_2	E_1
6	$\cos 6x$	A	A_1	A_1
6	$\sin 6x$	A	A_2	A_2
7	$\cos 7x$	A	B_1	E_1
7	$\sin 7x$	A	B_2	E_1
8	$\cos 8x$	A	A_1	E_2
8	$\sin 8x$	A	A_2	E_2
9	$\cos 9x$	A	B_1	B_1
9	$\sin 9x$	A	B_2	B_2
10	$\cos 10x$	A	A_1	E_2
10	$\sin 10x$	A	A_2	E_2

representation to which each function belongs) for the first few eigenfunctions of Eq. (49). For example, by choosing the A_1 irreducible representation of C_{2v} to represent the derivative operations, only the cosine functions with even eigenvalues are obtained.

We perform calculations for each symmetry group using various grid spacings. This is done to test the accuracy and the robustness of the SADAF representation. To evaluate the quality of these calculations we define

$$\epsilon = -\log_{10} \left(\frac{|\lambda_{calc} - \lambda_{exact}|}{|\lambda_{exact}|} \right), \quad (50)$$

which measures the number of significant figures in the calculated value, λ_{calc} , with respect to the true value, λ_{exact} .

In Table IV we present the results for the C_1 point group for 10 different grid sizes. For each grid we present the number of eigenvalues for which $\epsilon > 10$, 8 and 6 (i.e., the num-

TABLE IV. T_χ accuracy test for point group C_1 .

$\Delta\chi^a$	N_χ^b	$\epsilon > 10^c$	$\epsilon > 8^c$	$\epsilon > 6^c$
1.0	360	123	151	185
2.0	180	61	77	93
3.0	120	41	51	65
5.0	72	25	33	41
10.0	36	13	15	21
15.0	24	9	11	13
24.0	15	5	7	9
30.0	12	5	5	7
45.0	8	3	3	5
60.0	6	3	3	3

^aGrid spacing in degrees.

^bNumber of grid points.

^cThe numbers in these columns represent the number of eigenvalues obtained that have values of ϵ greater than 10, 8 and 6, respectively. (See Eq. (50).)

TABLE V. T_χ accuracy test for the point group C_{2v}

$\Delta\chi^b$	A_1^a							A_2^a						
	N_χ^c	$\epsilon > 10$	$\epsilon > 8$	$\epsilon > 6$	$\epsilon > 5$	$\epsilon > 4$	$\epsilon > 3$	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 5^d$	$\epsilon > 4^d$	$\epsilon > 3^d$
1.0	91	32 ^e	32 ^d	40 ^e	37 ^d	48 ^e	45 ^d	89	31 ^e	30 ^d	39 ^e	36 ^d	47 ^e	43 ^d
2.0	46	17	16	21	19	23	23	44	16	15	20	18	24	22
3.0	31	12	11	14	13	17	16	29	11	10	13	12	16	14
5.0	19	7	8	9	10	11	11	17	6	6	8	7	10	9
10.0	10	4	4	4	4	6	5	8	3	3	3	3	5	4
15.0	7	3	3	3	3	4	4	5	2	2	2	2	3	3
22.5	5	2	2	2	2	3	3	3	1	1	1	1	2	2

$\Delta\chi^b$	B_1^a							B_2^a						
	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 5^d$	$\epsilon > 4^d$	$\epsilon > 3^d$	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 5^d$	$\epsilon > 4^d$	$\epsilon > 3^d$
1.0	90	32 ^e	30 ^d	39 ^e	37 ^d	47 ^e	44 ^d	90	32 ^e	30 ^d	39 ^e	37 ^d	47 ^e	44 ^d
2.0	45	16	15	20	19	24	22	45	16	15	20	19	24	22
3.0	30	11	10	14	12	16	15	30	11	10	14	12	16	15
5.0	18	7	6	8	8	10	9	18	7	6	8	8	10	9
10.0	9	3	3	4	4	5	5	9	3	3	4	4	5	5
15.0	6	2	2	3	3	3	3	6	2	2	3	3	3	3
22.5	4	1	1	2	2	2	2	4	1	1	2	2	2	2

^aThe irreducible representation.^bGrid spacing in degrees.^cNumber of grid points.^dThe number of functions that have first derivatives accurate to the indicated level. (See the text for details.)^eThe number of eigenvalues within the indicated accuracy level.

ber of eigenvalues that match the exact eigenvalue up to 10 digits, 8 digits and 6 digits, respectively). Even for a grid spacing as large as 60 degrees (i.e., 6 points on the grid between 0 and 2π), we get 3 eigenvalues (half the total number of eigenvalues in this representation) accurate up to 10^{-10} or more. This is a clear indication of the robustness of the SADAF representation. For all the grids studied at least one-third of the eigenvalues were found to be accurate up to or beyond 10^{-10} .

In Table V we present results for the C_{2v} point group for irreducible representations A_1 , A_2 , B_1 and B_2 for 7 different grid sizes. The number of grid points in the A_1 irreducible representation is greater (by 2 additional points) than the number of grid points in the A_2 irreducible representation (for the same grid size) because unlike A_1 -irreducible representation functions, A_2 irreducible representation functions are zero at the end points of the grid, and consequently need not be sampled there. Similarly, the functions that transform according to the B_1 and B_2 irreducible reducible representations are zero at one of the end points of the grid and have a local extrema at the other. This is clear from the character table for C_{2v} .⁶⁴ Again, for the calculations for the C_{2v} point group, at least one-third of the eigenvalues are accurate up to or beyond 10^{-10} .

In Table VI we provide the results for the C_{6v} point group. Calculations are reported for 5 different grid sizes for the singly degenerate irreducible representations and 7 different grid sizes for the doubly degenerate irreducible representation. Here again a third of the eigenvalues are found to be accurate up to or beyond 10^{-10} .

B. Zero-potential tests: θ -dependence

To test the accuracy of the SADAF representation for the T_θ operator, consider Legendre's equation,

$$\left[-4 \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \theta} \right] P_l(\cos 2\theta) = 16l(l+1)P_l(\cos 2\theta), \quad (51)$$

where $P_l(\cos 2\theta)$ are the Legendre polynomials of order l and the operator on the left hand side of this equation is the T_θ operator, which is represented using the SADAF.

In Table VII we present results from direct diagonalization of the T_θ -SADAF representation matrix for 8 different grid sizes. Again, more than a third of the eigenvalues are accurate up to or beyond 10^{-10} .

V. COMPUTATIONAL TESTS FOR H_3^+ MOLECULAR ION—ROVIBRATIONAL STATES CALCULATIONS

The first observation of the infrared spectrum of H_3^+ was carried out in 1980.⁶⁵ Subsequent to this, accurate ground electronic potential energy surfaces of H_3^+ have been calculated^{38,66} which has stimulated a great amount of experimental^{67,68} and theoretical work (both quantum^{57,60–62} and semi-classical^{58,59,63}) to determine the rotational-vibrational eigenvalues of this molecule. This has made H_3^+ a benchmark system for new methods. However, even recently, questions have been raised regarding the spectrum of H_3^+ .⁶⁹

We use the analytical potential surface due to Meyer, Botschwina and Burton (MBB).³⁸ They performed *ab initio* calculations for 69 configurations of the H_3^+ molecular ion.

TABLE VI. T_χ accuracy test for the point group C_{6v} .

$\Delta\chi^b$	A_1^a							A_2^a						
	N_χ^c	$\epsilon > 10$	$\epsilon > 8$	$\epsilon > 6$	$\epsilon > 6$	$\epsilon > 6$	$\epsilon > 6$	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$
1.0	31	11 ^e	11 ^d	14 ^e	13 ^d	16 ^e	15 ^d	29	10 ^e	10 ^d	13 ^e	12 ^d	15 ^e	14 ^d
2.0	16	6	5	7	7	9	8	14	5	5	6	5	8	7
3.0	11	4	4	5	5	6	5	9	3	3	4	4	5	4
5.0	7	3	3	3	3	4	3	5	2	2	2	2	3	2
6.0	6	2	2	3	3	3	3	4	1	1	2	2	2	2
$\Delta\chi^b$	B_1^a							B_2^a						
	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$
1.0	30	11 ^e	10 ^d	13 ^e	12 ^d	16 ^e	14 ^d	30	11 ^e	10 ^d	13 ^e	12 ^d	16 ^e	12 ^d
2.0	15	5	5	7	6	8	7	15	5	5	7	6	8	7
3.0	10	4	3	5	4	5	5	10	4	3	5	4	5	5
5.0	6	2	2	3	2	3	2	6	2	2	3	2	3	3
6.0	5	2	2	2	2	3	2	5	2	2	2	2	3	2
$\Delta\chi^b$	E_1^a							E_2^a						
	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	N_χ^c	$\epsilon > 10^d$	$\epsilon > 8^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$	$\epsilon > 6^d$
1.0	30	21 ^e	20 ^d	26 ^e	25 ^d	31 ^e	29 ^d	60	21 ^e	20 ^d	26 ^e	24 ^d	32 ^e	29 ^d
2.0	30	11	10	13	12	16	15	30	11	10	14	12	16	14
3.0	20	7	7	9	8	11	10	20	8	7	9	8	11	10
5.0	12	5	4	5	5	7	6	12	4	4	6	5	7	6
6.0	10	4	3	5	4	5	5	10	4	4	4	4	6	5
10.0	6	2	2	3	3	3	3	6	2	2	2	2	4	3
15.0	4	1	1	2	2	2	2	4	2	2	2	2	2	2

^aThe irreducible representation.^bGrid spacing in degrees.^cNumber of grid points.^dThe number of functions that have first derivatives accurate to the indicated level. (See the text for details.)^eThe number of eigenvalues within the indicated accuracy level.

The highest energy configuration was $\sim 23000 \text{ cm}^{-1}$ above the bottom of the well. The global minimum in the ground electronic potential energy surface of H_3^+ corresponds to an equilateral triangle configuration. The surface has a D_{3h} point group symmetry. The zero-point energy on the MBB surface³⁸ is 4363.5 cm^{-1} . The ground electronic surface has a deep, narrow well (of magnitude $\sim 12000 \text{ cm}^{-1}$, measured from the bottom of the well) which supports a small number of widely spaced bound states. Above the well, the surface flattens considerably leading to an increase in the density of states and making the collinear configuration accessible.

TABLE VII. T_θ accuracy test.

$\Delta\chi^a$	N_χ^b	$\epsilon > 10^c$	$\epsilon > 8^c$	$\epsilon > 6^c$
1.0	90	35	42	49
2.0	45	17	20	24
3.0	30	12	14	17
5.0	18	7	8	11
9.0	10	4	5	6
10.0	9	4	5	6
15.0	6	3	3	4
22.5	4	2	2	3

^aGrid spacing in degrees.^bNumber of grid points.^cThe numbers in these columns represent the number of eigenvalues obtained that have values of ϵ greater than 10, 8 and 6, respectively. (See Eq. (50).)

Hence, large amplitude, floppy motions can be seen at energies greater than 12000 cm^{-1} from the bottom of the well.

The most detailed quantum-mechanical treatments of the rotational–vibrational eigenvalue problem of H_3^+ have been carried out by Whitnell and Light,^{60,61} Tennyson^{56,57} and Bacic and Zhang.⁶² Whitnell and Light used the full symmetry of the H_3^+ system to obtain a 3D-DVR-based representation of the APH Hamiltonian. The eigenvalues of the Hamiltonian matrix were obtained by using a successive truncation–diagonalization method. They constructed the full 3D Hamiltonian matrix using a basis that was generated from a series of reduced dimensionality 1D and 2D calculations. In many ways this is akin to neglecting off-diagonal elements to obtain blocks of the original 3D Hamiltonian matrix. That is, each block is diagonalized independently, and the eigenvectors are then used again to represent the full 3D Hamiltonian matrix. This new matrix is expected to be more sparse than the original full matrix, if the off-diagonal block-elements are small. Whitnell and Light used this idea to obtain a large number of states for total angular momentum $J=0$.

Tennyson and Henderson express the Hamiltonian using a single set of Jacobi coordinates. As discussed earlier in Sec. III, this coordinate system is not convenient for the treatment of the strong-interaction region in triatomic systems having D_{3h} point group symmetry. The reason for this is that the application of an element of this point group to a

single Jacobi coordinate results in the mixing of the other coordinates.⁴⁴ Tennyson and Henderson circumvent this problem by *not* using the full symmetry of the potential. (The symmetry they used was C_{2v} , whereas a surface for three identical atoms has a D_{3h} point group symmetry.) As a result, their matrices are larger than necessary. In their Jacobi-coordinate Hamiltonian, the angular part was represented using the DVR, whereas the two distance coordinates were represented using Finite Basis Representation (FBR). These investigators used their procedure to obtain a great number of states all the way up to dissociation (even though the Meyer, Botschwina and Burton potential is expected to be accurate only up to $\sim 23000 \text{ cm}^{-1}$ above the bottom of the well^{52,61} and the true dissociation is estimated at $\sim 35000 \text{ cm}^{-1}$ ^{56,70}).

Bacic and Zhang used all three sets of Jacobi coordinates to express the Hamiltonian as shown in Refs. 71–73. This enabled them to use the complete symmetry of the potential surface, but their basis set was correspondingly over-complete and hence nonorthogonal. They have used their method to obtain rotational–vibrational states of H_3^+ for total angular momenta $J=0$ and $J=1$.

A. Comparison of SADAF to earlier results

In this section, we obtain some of the bound eigenstates of H_3^+ (for $J=0$) to check the accuracy and computational effectiveness of the APH-SADAF Hamiltonian matrix. The MBB potential³⁸ is used because of the availability of previous results for comparison.^{56,57,60–62} Further, in this work we use a regular coordinate grid on which the APH-SADAF Hamiltonian matrix is obtained. Other methods, such as using surface functions to form the full 3D-Hamiltonian, are discussed elsewhere.⁷⁴ (It may be noted here that surface functions, while providing a solution to the two-dimensional θ - χ problem for fixed ρ , also provide a suitable “potential-adapted” basis to expand the full 3D-Hamiltonian. Hence, matrices obtained from using this technique may be expected to be smaller in size as compared to those obtained here from using a regular grid.)

Since the dimensionality of the problem is high (3D), the Hamiltonian matrix will also be large, and hence employing a direct diagonalization scheme to solve the corresponding eigenvalue problem is not viable. Instead, an iterative diagonalization technique can be used, a variety of which are available in the literature.^{54,55,75,22,23,76–79,18} All these techniques are based on the propagation of an initial vector by the application of a dynamical operator, which, in general, is a polynomial function of the Hamiltonian matrix, to obtain a Krylov-like basis. This basis representation of the Hamiltonian is then diagonalized to obtain an invariant subspace of eigenvectors. Some of these methods require the Hamiltonian matrix to be normalized, that is, to have eigenvalues only in the range $[-1, +1]$, which can be easily achieved using a method based on the L^2 -norm.⁸⁰

We use the Arnoldi iterative procedure^{53–55} which involves the repetitive application of the Hamiltonian matrix to an initial vector to form a basis set; the representation of the Hamiltonian in this new basis set leads to a Hessenberg form⁵³ for the Hamiltonian, which is relatively easy to diag-

TABLE VIII. Equivalence of irreducible representations of C_{6v} and D_{3h}

C_{6v}	D_{3h}
A_1	A'_1
A_2	A''_2
B_1	A'_1
B_2	A''_2
E_1	E''
E_2	E'

onalize. The action of the Hamiltonian matrix on any vector is calculated easily, taking advantage of the sparse structure of the APH-SADAF Hamiltonian matrix, which also obviates the need to store the full Hamiltonian matrix for this purpose. We do our calculations on a parallel computer (an IBM-SP2), so that many elements of the resultant vector are calculated simultaneously.

TABLE IX. Convergence of vibrational band origins of H_3^+ . The irreducible representation is A_1 in C_{6v} and A'_1 in D_{3h} .

	I	II	III	IV	V	VI	HT ^a
ρ_{min}^b	1.20	1.20	1.20	1.20	1.20	1.20	
ρ_{max}^b	5.20	5.20	5.20	5.20	5.20	5.50	
N_{θ}^c	16	16	24	32	48	64	
N_{χ}^d	45	90	90	90	90	90	
N_{χ}^e	7	13	13	13	13	13	
N^e	5040	18720	28080	37440	56160	74880	
1	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	[4363.5] ^g
2	9.6	9.4	0.0	0.0	0.0	0.0	3178.4
3	0.9	1.0	0.0	0.0	0.0	0.0	4777.0
4	30.1	30.1	0.0	0.0	0.0	0.0	6262.0
5	0.5	0.3	0.0	0.0	0.0	0.0	7282.5
6	3.5	3.5	0.0	0.0	0.0	0.0	7769.1
7	0.9	1.1	0.2	0.2	0.2	0.2	8996.6
8	4.8	0.7	0.0	0.0	0.0	0.0	9251.5
9	3.8	0.3	0.1	0.1	0.1	0.1	9964.0
10	18.7	0.2	0.1	0.1	0.1	0.1	10592.1
11	2.7	0.7	0.7	0.7	0.7	0.7	10913.1
12	6.8	0.4	0.4	0.4	0.4	0.6	11809.2
13	13.7	3.3	0.1	0.1	0.1	0.1	12145.8
14	3.5	0.8	1.0	1.0	0.1	0.9	12584.4
15		5.2	4.2	4.2	4.2	4.3	13284.7
16		40.0	40.0	40.0	40.1	39.9	13391.7
17		9.3	9.3	9.2	9.2	9.3	13705.4
18		4.5	4.6	4.6	4.6	4.6	14185.5
19		0.5	0.4	0.3		0.4	14662.6
20		4.4	4.7			4.5	14885.8
21		5.9	0.5			0.5	14938.6
22		29.1				29.4	15061.1
23		5.1				5.7	15158.3
24						2.4	15868.5
25						35.9	15909.3

^aReference 57. Authors used Jacobi coordinates with successive truncation-diagonalization scheme. (See the text.)

^bGrid points in ρ . N_{ρ} equally spaced points are chosen in the range $[\rho_{min}, \rho_{max}]$.

^cNumber of grid points in θ , chosen in the range $[0, \pi/2]$.

^dNumber of grid points in χ , chosen in the range $[0, \pi/6]$.

^eTotal number of grid points, $N = N_{\rho} N_{\theta} N_{\chi}$.

^fResults in these columns represent $|\text{this result} - \text{HT}|$ (in cm^{-1}).

^gZero-point energy (in cm^{-1}). All other values in this column are relative to this state.

TABLE X. Convergence of vibrational band origins of H_3^+ . Irreducible representation is A_2 in C_{6v} and A'_2 in D_{3h} .

	I	II	III	IV	V	VI	VII	HT ^a
ρ_{min}^b	1.20	1.20	1.20	1.2375	1.20	1.20	1.20	
ρ_{max}^b	5.20	5.20	5.20	4.2375	5.20	5.20	5.20	
N_ρ^b	16	16	16	48	24	24	32	
N_θ^c	45	90	90	60	80	90	90	
N_χ^d	5	5	9	5	11	11	11	
N^e	3600	7200	12960	14400	21120	23760	31680	
1	0.2 ^f	0.2 ^f	0.2 ^f	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	7492.6 ^g
2	3.5	3.5	3.5	0.1	0.1	0.0	0.0	10208.4
3	0.3	0.3	0.2	0.1	0.1	0.1	0.1	11525.4
4	5.4	5.4	5.4	0.0	0.1	0.1	0.0	12828.2
5	2.9	2.7	2.9	0.0	0.2	0.2	0.2	13746.7
6	3.1	2.8	3.1	0.1	0.1	0.1	0.1	14563.5
7	0.2	0.5	0.5	0.6	0.2	0.2	0.2	15178.1
8	15.6	15.6	15.7	0.0	0.1	0.0	0.0	15367.6
9	6.9	0.1	0.8	2.4	1.6	1.3	1.3	15950.8
10	50.4	5.6	0.4	17.7	11.1	8.4	11.5	16577.9
11	48.5	6.6	5.4	30.2	10.4	7.3	12.6	17076.8
12	4.6	17.3	13.7	0.1	2.4	1.7	1.7	17670.4
13	88.0	0.9	6.2	39.7	22.2	16.9	17.0	17805.3
14	102.2	102.9	46.1	5.0	4.7	4.0	4.3	17845.2
15	32.8	50.3	47.2	8.9	6.1	4.8	5.0	18316.0
16	150.5	17.2	13.3	60.7	25.2	18.4	18.5	18865.6
17	99.3	43.3	33.8	94.3	46.9	35.3	35.7	19173.8
18	11.7	8.1	32.4	18.7	14.1	14.2	14.2	19257.2
19	26.7	23.2	17.4	9.3	6.8	7.0	7.0	19720.6
20	1.1	6.7	0.5	4.1	3.2	3.4	3.4	20044.4
21	28.8	21.1	35.6	20.0	15.2	15.9	15.9	20268.9
22	5.3	0.9	19.9	14.0	10.8	11.4	11.4	20356.7
23	39.1	126.8	59.5	44.1	44.1	44.1	44.1	20806.9
24	33.1	68.0	38.0	29.4	29.6	29.6	29.6	20924.8
25	82.3	86.5	45.2	33.0	33.2	33.2	33.2	21174.7
26	13.0	12.2	10.5	21321.0				
27	177.8	112.6	89.7	21574.6				

^aReference 56. Authors used Jacobi coordinates with a successive truncation-diagonalization scheme. (See the text for details.)

^bGrid points in ρ . N_ρ equally spaced points are chosen in the range $[\rho_{min}, \rho_{max}]$.

^cNumber of grid points in θ , chosen in the range $[0, \pi/2]$.

^dNumber of grid points in χ , chosen in the range $[0, \pi/6]$.

^eTotal number of grid points, $N = N_\rho N_\theta N_\chi$.

^fResults in these columns represent $|$ this result $-HT|$ (in cm^{-1}).

^gRelative to zero-point energy in Table IX (in cm^{-1}).

Using this method we obtain the eigenstates of the Hamiltonian, one irreducible representation at a time. Since the point group used is C_{6v} the wavefunctions belong to the irreducible representations of this group. To obtain the corresponding representations in the D_{3h} point group, we first note that $D_{3h} \equiv C_{3v} \otimes C_s$, whereas, $C_{6v} \equiv C_{3v} \otimes C_2$.⁶⁴ Hence, the σ_h operation in D_{3h} is isomorphic to the C_2 operation in C_{6v} , which is associated with the parity of the wavefunction.³⁷ Based on this, a correspondence rule that maps the irreducible representations of D_{3h} onto the irreducible representations of C_{6v} can be derived. This rule is presented in Table VIII. Furthermore, since the parity of the wavefunction for $J=0$ is always even,³⁷ the only accessible states (for $J=0$) must belong to irreducible representations A_1 , A_2 or E_2 in the C_{6v} point group and A'_1 , A'_2 or E' in the D_{3h} point group.

In Tables IX, X and XI we provide results for different

TABLE XI. Convergence of vibrational band origins of H_3^+ . Irreducible representation E_2 in C_{6v} and E' in D_{3h} .

	I	II	III	IV	V	VI	HT ^a
ρ_{min}^b	1.20	1.20	1.20	1.20	1.20	1.20	
ρ_{max}^b	5.20	5.20	5.20	5.20	5.20	5.20	
N_ρ^b	16	32	16	16	24	24	
N_θ^c	45	45	90	90	80	90	
N_χ^d	12	12	12	20	24	24	
N^e	8640	17280	17280	28800	46080	51840	
1	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	0.0 ^f	2521.3 ^g
2	0.4	0.1	0.4	0.4	0.1	0.1	4997.4
3	2.6	0.0	2.6	2.6	0.0	0.0	5553.7
4	0.4	0.0	0.5	0.5	0.1	0.1	7003.4
5	0.1	0.0	0.0	0.0	0.0	0.0	7868.7
6	41.5	0.0	41.5	41.5	0.1	0.1	8487.0
7	5.2	4.6	0.5	0.5	0.7	1.1	9107.6
8	4.1	0.2	4.3	4.3	0.1	0.0	9650.6
9	5.7	0.1	5.8	5.8	0.0	0.0	9996.5
10	6.0	0.2	6.1	6.1	0.0	0.0	10642.6
11	1.2	0.7	0.3	0.3	0.9	0.8	10853.3
12	30.2	0.0	30.2	30.2	0.4	0.4	11321.5
13	17.6	15.9	2.0	2.0	3.9	3.2	11651.1
14	6.0	1.3	4.0	4.0	1.0	0.9	12073.2
15	6.2	3.3	0.7	0.7	4.5	3.8	12294.2
16	7.6	0.6	8.2	8.1	3.5	2.9	12467.5
17	17.3	2.9	22.6	22.6	1.9	1.6	12694.0
18	43.3	1.1	45.1	45.1	0.4	0.3	13313.4
19	5.1	14.9	15.0	15.0	2.3	1.7	13385.1
20	27.0	1.4	21.8	21.7	24.7	25.2	13553.4
21	70.4	65.1	12.8	12.5	11.2	8.4	13680.9
22	0.1	244.1	1.1	1.1	1.1	1.1	14052.2
23	7.8	26.2	1.5	1.2	1.2	1.2	14210.9
24	2.7	7.6	13.2	14.64.7			
25	29.5	17.0	13.7	14878.0			
26	2.4	1.0	0.8	14885.6			

^aReference 56. Authors used Jacobi coordinates with a successive truncation-diagonalization scheme. (See the text for details.)

^bGrid points in ρ . N_ρ equally spaced points are chosen in the range $[\rho_{min}, \rho_{max}]$.

^cNumber of grid points in θ , chosen in the range $[0, \pi/2]$.

^dNumber of grid points in χ , chosen in the range $[0, \pi/6]$.

^eTotal number of grid points, $N = N_\rho N_\theta N_\chi$.

^fResults in these columns represent $|$ this result $-HT|$ (in cm^{-1}).

^gRelative to zero-point energy in Table IX (in cm^{-1}).

grid sizes for the A_1 , A_2 and E_2 irreducible representations (in the C_{6v} point group), respectively. The stress in this study is not on obtaining many states, but instead to understand how the accuracy of the states obtained is affected by a change in the number of grid points. In Tables IX, X and XI we present results, respectively, for all A_1 -states up to $\sim 16000 \text{ cm}^{-1}$, all A_2 -states up to $\sim 22000 \text{ cm}^{-1}$ and all E_2 -states up to $\sim 15000 \text{ cm}^{-1}$ above the absolute energy minimum of the MBB surface (which is approximately half-way to dissociation). These states extend above the triangle to linear conformational change barrier (which occurs roughly at $\sim 12000 \text{ cm}^{-1}$), and hence describe a number of states associated with large-amplitude floppy motions.

For our calculations, the absolute minimum of the potential was at ~ -0.1857 atomic units, where the zero of the potential was set at 0.02 atomic units above the estimated^{56,71} dissociation limit. Hence, we did not sample in regions

where the potential was very much above dissociation since the MBB potential is considered to be accurate only up to 23000 cm^{-1} above the bottom of the well^{38,61} (which is roughly three-quarters of the way to dissociation). This restricts ρ_{min} and ρ_{max} (the range in the ρ -coordinate), values for which can be found in the tables. Diagonalizing the full Hamiltonian did produce some complex eigenvalues (due to the nonhermiticity of the Hamiltonian matrix). But since these were due to the discretization scheme (and hence non-physical), their absolute values were always found to be higher than the physically significant (real) eigenvalues. Furthermore, they were not stable. Increasing the number of grid points in the θ -coordinate makes these physically insignificant complex eigenvalues occur at even higher absolute values. Thus, we considered a relatively large number of grid points in θ , as seen in Tables IX, X and XI.

The number of grid points required in the ρ and χ coordinates, for convergence, was found to be relatively small. It was found that 24 grid points in the ρ -coordinate produced adequately accurate eigenvalues in most cases. Similarly, the χ -coordinate also required fewer grid points.

From the tables, it is clear that the calculated eigenstates are, generally, more accurate with increased sampling, as is to be expected. However, a couple of exceptions exist, where eigenvalues were not as accurate as the others. For example, the 16th eigenvalue in Table IX, which although is within 0.5% of Tennyson's value, is not as accurate as the others. An exhaustive study in this regard has not been conducted.

We found that for the Arnoldi iterative diagonalization technique the convergence rate decreased as the size of the matrix increased. Such behavior has been observed previously,⁵³ and typically results when the initial vector has too small an overlap with the desired eigenstates; in such cases a random initial vector was chosen, but this does not completely resolve the problem as the size of the matrix increases. A more robust approach is to use a polynomial pre-conditioning method⁸³ to obtain a good starting vector, and we will use this method in future studies.

B. Computational scaling of the SADAF Hamiltonian matrix-Arnoldi vector operation

From Eqs. (31)–(33) it is clear that the $J=0$ APH Hamiltonian may be written as the direct product of matrices in ρ , θ and χ . Hence, the operation of the full Hamiltonian matrix on a vector scales as $N[\min[N_\rho, W_\rho] + \min[N_\theta, W_\theta] + \min[N_\chi, W_\chi]]$, where N_ρ , N_θ and N_χ are the number of grid points in ρ , θ and χ respectively, W_ρ , W_θ and W_χ are the related to the band-width of the DAF in ρ , θ and χ and $N=N_\rho N_\theta N_\chi$. If we assume that $N_\rho \approx N_\theta \approx N_\chi$, then the Hamiltonian matrix-Arnoldi vector operation scales as $N^{4/3}$ for small N and scales linearly for large N .

VI. CONCLUSIONS

In this paper we have shown how Symmetry-Adapted Distributed Approximating Functionals can be formed. These can be used to obtain accurate derivatives of appropriately symmetric functions. The symmetry of the function is fully utilized in constructing the derivative operator.

We have used SADAFs to represent the Pack–Parker triatomic APH coordinate kinetic energy operator. Although, we have used a regular coordinate grid to obtain the coordinate representation for the APH Hamiltonian, this does not necessarily have to be the case. We demonstrate elsewhere⁷⁴ that surface functions could be obtained and used for a ‘‘potential-adapted’’ (coordinate) representation of the Hamiltonian. Alternatively, as stated in Sec. II, one could obtain an approximation to the action of the SADAF operator on a function either on an irregular grid or by using Monte Carlo sampling.

The eigenvalue problems that result from constructing the SADAF representation of the Hamiltonian are solved using an Arnoldi iterative scheme. We find this method to converge slowly for large matrix size, as has been documented elsewhere.⁵³ The number of Arnoldi vectors necessary to obtain the eigenstates increases rapidly with the size of the problem. In the future, we hope to circumvent this problem by using a polynomial preconditioning of the starting vector.⁸¹

We conclude that the SADAF representation, making use of the C_{6v} potential symmetry of three like atoms (in the APH coordinate system), can be used to obtain an efficient computational algorithm to calculate ro-vibrational bound states. Consequently, the SADAF representation should be very useful in performing bound-state/scattering calculations and in solving various other partial differential equations.^{82,83}

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