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HO_2 Ro-Vibrational Bound-State Calculations for Large Angular Momentum: $J = 30$, 40, and 50[†]

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The Lanczos homogeneous filter diagonalization method and the real Chebyshev filter diagonalization scheme incorporating doubling of the autocorrelation functions have been employed to compute the HO_2 ro-vibrational states for high total angular momenta, $J = 30$, 40, and 50. For such computationally challenging calculations, we have adopted a parallel computing strategy to perform the matrix−vector multiplications. Low-lying bound states and high-lying bound states close to the dissociation threshold are reported. For low-lying bound states, a spectroscopic assignment has been attempted and the widely used approximate J-shifting method has been tested for this deep-well system. For high-lying bound states, the attempted spectroscopic assignments as well as the J-shifting approximation fail because of very strong Coriolis mixing, indicating that the Coriolis couplings are important for this system.

1. Introduction

Exact nonzero total angular momentum ($J > 0$) calculations are essential in fully understanding quantum reaction dynamics and in correctly simulating molecular spectroscopy. For example, in unimolecular dissociation, to understand the temperature variation of rate constants, it is important to implement many $J > 0$ calculations as accurately as possible. In bimolecular reactions, the detailed cross sections can only be obtained after summing over many manifolds of scattering matrix elements associated with nonzero J. When assigning experimental molecular spectra, it is necessary to compute exactly the ro-vibrational states involved. However, these $J > 0$ calculations are still very challenging even for triatomic reactions, especially when dealing with complex forming systems. The major reason for this situation is the so-called "angular momentum catastrophe":[1] many $J > 0$ calculations have to be performed, and the size of the Hamiltonian matrix increases linearly with J. For these nonzero J calculations, it is apparently impractical to employ conventional direct diagonalization methods because of the extensive computer core memory needed. Several sophisticated basis-set contraction schemes[2,3] do exist, but because of their unfavorable scaling they are limited to optimized basis sets of $N < 10\,000$. Variational approaches can be used to compute the low bound states accurately, but for high-lying bound states, convergence becomes difficult with the increasing size of the basis set.[4,5] Iterative methods such as the real Chebyshev iterative method[6−8] and the Lanczos method[9,10] are well suited to solving this type of large-scale eigenvalue problem and in recent years have become increasingly popular. The preconditioned inexact spectral transformation method developed recently by Carrington and co-workers is a promising variant of these methods that can reduce the required number of iterations substantially at high energies.[11−13] Combination methods such as the two-layer Lanczos iteration approach introduced by Yu[14] and the contracted basis-iterative method introduced by Carrington and co-workers[15] also represent promising recent numerical developments. These methods are useful, especially for large basis sets, because they do not require explicit storage of the Hamiltonian matrix. Rather, only the multiplication of the Hamiltonian onto a vector is required. When combined with a sparse representation of the Hamiltonian, such as a discrete variable representation (DVR),[16] both memory and CPU time can be reduced dramatically.

Lanczos methods exploit the advantages of the tridiagonal structure of the Lanczos subspace Hamiltonian, which is generated by the iterative Lanczos algorithm.[9] Although the Lanczos algorithm has been used commonly for matrix diagonalization[10] and short-time propagations,[17] recent work in the Brisbane lab has focused on exploring more general applications of the Lanczos representation, including spectral densities,[18−20] filter diagonalization for high-lying bound states and resonances,[21−26] partial resonance widths in unimolecular decay,[27] and state-to-state reactive scattering.[28,29] An important feature of these newer Lanczos implementations is that all physically relevant information is extracted from within the Lanczos representation. This allows a single Lanczos iteration of arbitrary length to be utilized for the propagation rather than a sequence of short iterations. We note that for scattering or resonance applications the absorbing boundary conditions are imposed within the Lanczos algorithm by incorporation of a complex absorbing potential (CAP) into the Hamiltonian. Consequently, the Lanczos iterations are complex and yield a complex-symmetric tridiagonal representation of the Hamiltonian, although as is well known (e.g., ref 13) the complex-symmetric Lanczos approach is numerically less stable than its real or Hermitian counterparts. Significant progress has also been made recently in the search for a real Lanczos subspace method capable of computing state-to-state reactive scattering probabilities.[30−32]

Another powerful iterative method is the real Chebyshev method, which is attractive from both computational time and computer memory points of view. Its origin lies with the early work of Tal-Ezer and Kosloff,[33] in which the evolution operator $\exp(-i\hat{H}t/\hbar)$ is expanded in terms of Chebyshev polynomials. Subsequently, very important developments were made by several research groups. Kouri and co-workers[34−39] derived a

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new time-independent (TI) wave packet Lippmann−Schwinger equation and presented Chebyshev expansion expressions for both the Green operator and the Dirac delta function. Mandelshtam and Taylor[40−42] introduced a real damping scheme into the Chebyshev recursion, which made the real wave packet method possible for dissipative systems. The real Chebychev propagation method can be viewed in an alternative way as a modification of the time-dependent Schrödinger equation. In this respect, two related (discrete/continuous time) forms of the modified equations have been proposed by Chen and Guo[43] and more generally by Gray and Balint-Kurti.[44] These various real wave packet approaches have been applied successfully to different fields such as bound- or resonance-state calculations,[6,7,45] reactive scattering,[46−48] and surface scattering.[49,50] For bound-state calculations, it is possible to exploit the doubling scheme to compute autocorrelation functions, which will double the efficiency of the real Chebyshev iteration. For resonance computations, Li and Guo intuitively proposed that the scheme of doubling Chebyshev correlation functions should still be valid,[51] even if the damped Chebyshev recursion is adopted, with numerical validation of their proposal for several molecular systems.[51,52] Recently, Neumaier and Mandelshtam derived a pseudo-time Schrödinger equation and provided rigorous proof that an exact doubling formula exists for damped Chebyshev propagation.[53] It is Neumaier and Mandelshtam's newest doubling scheme, in combination with their low storage filter diagonalization strategy[6] (DS/LSFD), that we will employ to calculate the challenging $J = 30$, 40, and 50 low- as well as high-lying bound states of the HO_2 system in this paper. The most important advantage associated with this approach is that one can employ a real algorithm with a single, extended Chebyshev vector recursion. The doubling scheme[51,53] for calculating Chebyshev correlation functions leads to further efficiency in comparison with propagation of a complex wave packet. Of course, the computational tasks are still too heavy using a conventional single-processor calculation for the high angular momentum cases studied in this work, in particular for the high-lying bound states. Thus, we adopt a parallel computing model herein.

The reasons for employing parallel computing are twofold. On one hand, the CPU time required to compute the high-lying bound states for this system is substantial, partly because of the deep potential well corresponding to the HO_2 complex, which supports hundreds of bound states for the $J = 0$ case. As J increases, the number of bound states will increase linearly with J, which makes the convergence more difficult. On the other hand, the storage requirement of the potential matrix and overlapping integrals also increases linearly with J. Thus, with typical memory available on current cluster machines (i.e., a few GBytes per node), the employment of parallel computing strategies becomes unavoidable for higher J values. Recently, several groups have begun to exploit the power of parallel computing in performing the rigorous $J > 0$ quantum dynamics calculations in TD wave packet methods and in sequential diagonalization and truncation methods.[54,55] In this paper, we show how such parallel computations make it possible to compute the dense ro-vibrational state manifold with computational times and storage requirements comparable to the $J = 0$ case. Our specific implementation involves a message-passing interface (MPI)[56] inserted in our local Fortran programs utilizing the real Chebyshev and Lanczos methods.

We note that although the present paper deals only with bound states at large angular momenta our calculations are carried out with explicit incorporation of dissipative boundary conditions (i.e., the complex-symmetric Lanczos algorithm and the real damped Chebychev propagation) because this allows the output of the calculations to be analyzed further to investigate resonance structure above the dissociation threshold. Such analysis of the continuum part of the spectra is, however, beyond the scope of the current paper.

The HO_2 system is very important in combustion chemistry and atmospheric chemistry[57] and hence has been studied extensively from both theoretical and experimental perspectives. However, even this seemingly simple system involving only three atoms turns out to be very difficult to model quantum mechanically. Unlike the H_3 or H_2F (or their isotopes) systems, see, for example, refs 58−60, the agreement between theory and experiment, and even among different theories and different experiments, has not yet reached a quantitative level for HO_2. The reader is referred to Wolfrum for some detailed comparisons.[61] The potential energy surfaces (PES) used most are those by Melius and Blint,[62] Varandas and co-workers,[63] Kendrick and Pack,[64] and Troe and co-workers[65,66] (we note that accurate ab initio surfaces further adjusted to fit experimental spectroscopic data have been reported[4] and that very recently a new global ab initio PES for the HO_2 ground state has been developed[67]). Although most of the calculations have focused on the $J = 0$ case because of obvious computational difficulties, $J > 0$ calculations have begun to appear in recent years. Among them, Goldfield's group[46,68,69] has performed exact calculations of the initial-state-resolved reaction probability at several J values for the bimolecular reaction $H + O_2 \rightarrow OH + O$. $J > 0$ calculations have been reported for the low-lying bound states by Wu and Hayes.[70] Also notable is the work of Bunker et al. in which a variational method has been employed to converge bound states up to 1.0 eV above the zero point level for some high J values (refs 4 and 5 and private communications). We have recently utilized the Lanczos homogeneous filter diagonalization (LHFD) method as well as the real Chebyshev method to compute bound states for $J = 1−6$, 10, and 20 as well as the resonance eigenvalues, which yield the quantum-specific rate constants, $k(E,J)$.[71−73] Some comparisons have been presented therein between the quantum rates and Troe et al.'s statistical results.[65,66] The range of the angular momenta that are relevant to the thermal rate up to 5000 K is from $J = 0$ to at least $J = 60$.[65]

Because of the computational challenges of the exact calculations, approximate quantum methods such as adiabatic rotation (AR),[74] J-shifting,[75] and helicity-conserving (HC)[76] approximations are used commonly for nonzero J calculations. As important as exact quantum methods may be, approximations may become unavoidable for complex and/or large systems. Therefore, it is of interest to compare the exact quantum results with different approximate methods. For complex-forming reactions such as the HO_2 system, Coriolis coupling is important because of the large amount of flexibility in the molecule at high energies, and such approximations might cause significant inaccuracies. Another motivation of this paper is to test these approximations, for example, J-shifting, for such high J values and to investigate when and how it fails. The key issue in these approximations is whether a reasonably good quantum number, Ω, associated with the projection of total angular momentum on a body fixed axis exists. If the substates, Ω , of the wave function for $J > 0$ are heavily coupled, then the Coriolis coupling between the states cannot be ignored and any attempts to assign the helicity quantum number, Ω, will fail. We will examine this issue by comparing the exact quantum results with a rationally implemented J-shifting approximation and a helicity quantum number, Ω, assignment for both spectroscopic symmetry calculations of bound states. If this assignment is successful, then the approximate calculations may be applied, otherwise the Coriolis coupling should not be ignored and exact quantum methods have to be used.

The remainder of this article proceeds as follows. In Section 2 we describe the theoretical methods needed to characterize bound states for nonzero total angular momentum, together with a parallel computing model in brief. In Section 3 we provide computational details and then present the results of $J = 30$, 40, and 50 bound-state calculations performed on the HO_2 system. Detailed comparisons with previous work for the lower bound-state manifold with $J = 30$ as well as the comparisons with *J*-shifting approximation will also be given in Section 3. Section 4 concludes.

2. Methodology

2.1. Representation. The three internal Jacobi coordinates (R,r,γ) are described with discrete variable representations (DVRs), whereas the three Eulerian angles (θ,ϕ,ψ) are described with a finite basis set.[77−79] This procedure is very efficient because the potential part of the Hamiltonian matrix is diagonal, which can reduce the memory requirement substantially. The triatomic Hamiltonian in Jacobi coordinates in a body fixed frame is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^{\,2}}{2\mu R^2} + \frac{\hat{j}^2}{2\mu r^2} + V(R,r,\gamma) \tag{1}$$

where orbital angular momentum, $\hat{l}^{\,2} = (\hat{J} - \hat{j})^2 = \hat{J}^2 + \hat{j}^{\,2} - 2\hat{J}\cdot\hat{j}$. To reduce the six-dimensional (6D) Hamiltonian to a four-dimensional (4D) one for each single J value, we use a symmetric top eigen function to expand the total wave function. Multiplying the Hamiltonian on the left side by $\langle D^J_{M\Omega}(\phi,\theta,\psi)|$, one can obtain the coupled equations of motion. Here J is the total angular momentum quantum number, and quantum number M is the projection of total angular momentum onto the space-fixed z axis. The derivations use the basic definitions of Wigner D functions and some integral formulas. Although the details of the derivation are very tedious, we will only give the final results of the coupled equations as follows

$$\hat{\mathrm{H}}_{\Omega,\Omega} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + V(R,r,\gamma) + \left(\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2}\right)\left(-\frac{\hbar^2}{\sin\gamma}\frac{\partial}{\partial\gamma}\sin\gamma\frac{\partial}{\partial\gamma} + \frac{\hbar^2\Omega^2}{\sin^2\gamma}\right) + \frac{\hbar^2}{2\mu R^2}\left[J(J+1) - 2\Omega^2\right] \tag{2}$$

and

$$\hat{H}_{\Omega,\Omega\pm1} = (1 + \delta_{\Omega,m})^{1/2}\frac{\hbar^2}{2\mu R^2}\sqrt{J(J+1) - \Omega(\Omega\pm1)}\left[\pm\frac{\partial}{\partial\gamma} + (\Omega\pm1)\cot\gamma\right] \tag{3}$$

with $m = 0$ for $\hat{H}_{\Omega,\Omega+1}$ and $m = 1$ for $\hat{H}_{\Omega,\Omega-1}$. Such coupled equations can be represented in DVR

$$H^{\lambda'\Omega'}_{\lambda\Omega} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} + V(R,r,\gamma^{\Omega}_{\lambda})\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} + \left(\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2}\right)\sum_j T^{\Omega}_{j\lambda}[\,j(\,j+1)\hbar^2]\,T^{\Omega}_{j\lambda'}\delta_{\Omega'\Omega} + \frac{\hbar^2}{2\mu R^2}\left[J(J+1) - 2\Omega^2\right]\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} + \sum_j T^{\Omega}_{j\lambda}t^{Jj}_{\Omega,\Omega+1}T^{\Omega+1}_{j\lambda'}\delta_{\Omega'\Omega+1} + \sum_j T^{\Omega}_{j\lambda}t^{Jj}_{\Omega,\Omega-1}T^{\Omega-1}_{j\lambda'}\delta_{\Omega'\Omega-1} \tag{4}$$

with

$$t^{Jj}_{\Omega,\Omega\pm1} = -(1 + \delta_{\Omega,m})^{1/2}\frac{\hbar^2}{2\mu R^2}\sqrt{J(J+1) - \Omega(\Omega\pm1)}\sqrt{j(j+1) - \Omega(\Omega\pm1)}.$$

In eq 4, we have used Ω-dependent DVR for the γ coordinate, which is obtained by either diagonalizing the coordinate operator ($x = \cos\gamma$) matrix

$${}^{\Omega,\gamma}\Delta_{jj'} = \int_{-1}^{1}\Theta^{\Omega}_{j}(\gamma)\,x\Theta^{\Omega}_{j'}(\gamma)\,\mathrm{d}x$$

or by a Gauss−Jacobi quadrature scheme

$${}^{\Omega,\gamma}\Delta_{jj'} = \int_{-1}^{1}W(x)\,\tilde{\Theta}^{\Omega}_{j}(\gamma)\,x\tilde{\Theta}^{\Omega}_{j'}(\gamma)\,\mathrm{d}x.$$

Here $\Theta^{\Omega}_{j}(\gamma)$ is the associated Legendre polynomial, $W(x) = (1 - x^2)^{\Omega}$ is the weight function, and

$$\tilde{\Theta}^{\Omega}_{j}(\gamma) = \Theta^{\Omega}_{j}(\gamma)/\sqrt{(1 - x^2)^{\Omega}}.$$

In the Gauss−Jacobi quadrature scheme, the transformation matrix is set up according to

$$T^{\Omega}_{j\lambda} = \sqrt{\omega_\lambda}\,\tilde{\Theta}^{\Omega}_{j}(x_\lambda).$$

Here λ is used to label the DVR in the γ coordinate, and x_λ and ω_λ are the quadrature points and weights, respectively, which can be obtained from standard methods.[80] In the direct diagonalization scheme, the DVR points and the transformation matrix are simply the eigenvalues and the eigenvector matrix of the coordinate operator matrix. We have compared the two DVR schemes, and the DVR points as well as the transformation matrix, T, from the two methods are nearly the same. For R and r coordinates, we have used potential-optimized DVR.[81] The details of the DVRs will be given in Section 3.

2.2. Propagation. In the iterative Chebyshev method, the basic propagation is a three-term recursion. In their modified version of Chebyshev propagation, Mandelshtam and Taylor[40−42] proposed a real damped Chebyshev polynomial recursion to impose the outgoing boundary conditions. Because the damping operator is introduced in the recursion, the doubling property of the original Chebyshev recursion to compute the autocorrelation functions would seem at first glance to be inapplicable. However, as pointed out by Li and Guo,[51] the original doubling scheme can still be adapted to calculate narrow resonances, albeit in an approximate way. Neumaier and Mandelshtam[53] subsequently provided a rigorous proof that an exact doubling scheme exists for damped Chebyshev propagation. The new damped Chebyshev propagation then becomes

$$\xi^{\hat{W}}_{k+1} = D(\hat{W})^{-1}(2\hat{\mathrm{H}}_{\mathrm{norm}}\xi^{\hat{W}}_{k} - \xi^{\hat{W}}_{k-1}) \tag{5}$$

Here $\xi_0^{\hat{W}} = \Phi_0$ is the initial real random wave packet, and $\xi_1^{\hat{W}} = 0$. $\hat{D}(\hat{W}) = 1 + 2\hat{W}$, and $\hat{W}$ is the absorbing potential. $\hat{H}_{\mathrm{norm}} = (\hat{H} - \bar{H})/\Delta H$ with $\bar{\mathrm{H}} = 0.5(H_{\max} + H_{\min})$ and $\Delta H = 0.5(H_{\max} - H_{\min})$. The new doubling formula is as follows

$$c_{2k} = (\xi_k^{\hat{W}}|\xi_k^{\hat{W}}) - (\xi_{k+1}^{\hat{W}}|D(\hat{W})|\xi_{k+1}^{\hat{W}}) \tag{6a}$$

$$c_{2k-1} = (\xi_k^{\hat{W}}|\xi_{k-1}^{\hat{W}}) - (\xi_{k+1}^{\hat{W}}|D(\hat{W})|\xi_k^{\hat{W}}) \tag{6b}$$

where the (•|•) denotes the complex nonconjugate inner product. Such a doubling scheme can allow us to save the number of Chebyshev iterations by a factor of 2, which is especially useful for the heavy computational tasks such as the high J value cases in this paper. The autocorrelation functions need to be stored in the Chebyshev propagation for later FD analysis.

Similarly, in the Lanczos iteration, we choose a normalized, randomly generated initial vector, $v_1 \neq 0$, and set $\beta_1 = 0$ and $v_0 = 0$. Then we use the basic Lanczos algorithm for complex-symmetric matrices[82]

$$\beta_{k+1} v_{k+1} = \hat{H}' v_k - \alpha_k v_k - \beta_k v_{k-1} \tag{7}$$

to project the non-Hermitian absorbing potential augmented Hamiltonian into a Krylov subspace. The $M \times M$ tridiagonal representation of the Hamiltonian, T_M, has diagonal elements, $\alpha_k = (v_k|\hat{H}'|v_k)$, and subdiagonal elements, $\beta_k = (v_{k-1}|\hat{H}'|v_k)$. Note that a complex-symmetric inner product is used (i.e., bra vectors are not complex conjugated). Again, the two vectors, $\{\alpha\}$ and $\{\beta\}$, are stored in Lanczos iterations for later FD analysis to extract physical information such as bound-state or resonance quantities.

Though conceptionally simple, the propagation is the most time-consuming part of the calculation, and Hamiltonian matrix−vector multiplications will be repeated for many times. We use MPI to perform parallel computation for the matrix−vector multiplications. For even spectroscopic symmetry, the 4D matrix−vector multiplication looks like

$$\begin{pmatrix} H_{00} & H_{01} & 0 & 0 \\ H_{10} & H_{11} & H_{12} & 0 \\ 0 & H_{21} & H_{22} & \ddots \\ 0 & 0 & \ddots & \ddots \end{pmatrix} \begin{pmatrix} \psi_{\Omega=0} \\ \psi_{\Omega=1} \\ \psi_{\Omega=2} \\ \vdots \end{pmatrix} = \begin{pmatrix} \phi_{\Omega=0} \\ \phi_{\Omega=1} \\ \phi_{\Omega=2} \\ \vdots \end{pmatrix} \tag{8}$$

with, $\phi_\Omega = H_{\Omega,\Omega-1}\psi_{\Omega-1} + H_{\Omega,\Omega}\psi_\Omega + H_{\Omega,\Omega+1}\psi_{\Omega+1}$. For odd spectroscopic symmetry, the Hamiltonian matrix is the same except $\Omega = 1, 2, ..., J$. The spectroscopic symmetry parity is defined as $(-1)^{J+p}$, with p being the parity of the total 6D wave function under inversion of the space-fixed nuclear coordinates. We adopt a natural way to distribute the problem with respect to the Ω blocks, which makes the calculations of autocorrelations or $\{\alpha\}$ and $\{\beta\}$ much easier and necessitates only minimal modifications of the code for parallel computing. We assign one processor as master processor (ID = 0), which is used to write autocorrelation functions or $\{\alpha\}$ and $\{\beta\}$ and assign all other processors as working processors for performing the matrix−vector multiplications for different Ω components. Our implementation has the flexibility that any number of cpus ($2 \leq n \leq J + 2$) in a cluster machine can be employed. According to the Coriolis coupling rules, only two nearest-neighbor Ω components need to communicate, and we use the MPI_SEND and MPI_RECEIVE commands to carry out such communications. In this way the data transfer between processors is not too heavy. We distribute the work load as equally as possible over processors. However, because $j_{\min}$ is different for each Ω component, but $j_{\max}$ is the same, that is, the DVR size for γ is different for each Ω component, and for the highest or the lowest Ω components, only one Coriolis coupling term is required; thus, the load for each processor is still not perfectly balanced. Indeed, in distributed computing, there is always a tradeoff between load balance and complexity in coding. Our principle is that strict balance is not absolutely necessary, but for the present application the balancing works out quite well in general. We note that other parallel models have been used to calculate ro-vibrational states. For example, Wu and Hayes[70] defined a conceptional 3D mesh where Ω is used as one of the indices, Mussa and Tennyson[55] have employed a two step procedure, and Eggert et al.[83] described a fine granularity parallel Lanczos calculation in which a pseudo spectral split Hamiltonian scheme has been employed to implement the action of the Hamiltonian on the wave function. Here different parallel strategies are employed to suit the different methods and different machines.

2.3. Extraction of Relevant Information. In the LSFD method, given the discrete correlation function, c_k, one can employ evolution operator, $\hat{U}$, to set up a small-sized generalized eigen equation.[6] Solution of the generalized eigen equation will give all of the information for both bound states and resonances. The reader is referred to Mandelshtam and Taylor's work for more details.[6,7] In the LHFD method, we perform filter diagonalization within the Krylov subspace representation to extract the bound and resonance information for any chosen energy windows. A key issue in LHFD is solving the homogeneous linear system by using an efficient backward three-term substitution recursion. The details of LHFD have been given previously.[25,27]

3. Results

3.1. Computational Details for the HO_2 System. The triatomic HO_2 Hamiltonian matrix was set up in terms of reactant Jacobi coordinates, and the HO_2 DMBE IV PES[63] was employed as we have done previously for $J = 0{-}6$, 10, and 20 bound-state and resonance calculations.[25−27,71−73] For the two radial coordinates, a potential-optimized DVR[81] (PODVR) was utilized to reduce the size of the Hamiltonian matrix. For the R coordinate, we have used $N_R = 110$ PODVR points, which were contracted from 315 evenly spaced primitive sinc DVR points[84] spanning the range from 0.5 a_0 to 11.0 a_0 with the one-dimensional reference potential, $V(R,r_e,\theta_e)$. Similarly, for the r coordinate, $N_r = 50$ PODVR points were obtained from 150 primary DVR points spanning the range from 1.3 a_0 to 5.0 a_0 using the reference potential, $V(R_e,r,\theta_e)$. For the γ variable, Ω-dependent symmetry-adapted DVR functions, defined by correspondingly associated Gauss−Jacobi quadrature points, were employed to take account of the odd O−O exchange parity. Another kind of symmetry originated from the Wigner D functions; that is, spectroscopic symmetry, has also been considered. The resulting direct product basis set was further contracted by discarding those points whose potential energies were higher than the cutoff energy, $V_{\mathrm{cutoff}} = 4.016$ eV, resulting in the final basis size of approximately 110 700($J + 1$) for even spectroscopic symmetry and approximately 110 700 × J for odd spectroscopic symmetry. This basis-set size has been tested carefully for convergence for the $J = 0$ case and is then carried over to the $J > 0$ cases. For example, for $J = 0$ we have doubled the grid size for the angular coordinate while keeping the other two (R,r) grid sizes fixed and found that only the sixth digit of bound-state energies varies. Hence, the degree of convergence with respect to basis set parameters is on the order of five digits. We note the issue raised in ref 85 of using an equilibrium value

TABLE 1: Selected Low Bound-State Energies for $J = 30$ and Even Spectroscopic Symmetry from DS/LSFD, LHFD, Bunker et al.'s Variational Calculations, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	Bunker	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.124642	.124642	.124498	0.125357	0	30	(0,0,0)
2	.125728	.125729	.125617	0.127746	1	30	(0,0,0)
3	.135318	.135319	.135005	0.134914	2	29	(0,0,0)
4	.146785	.146786	.146458	0.146859	3	28	(0,0,0)
5	.163396	.163396	.162959	0.163583	4	27	(0,0,0)
6	.184702	.184702	.184127	0.185085	5	26	(0,0,0)
7	.210661	.210659	.209911	0.211365	6	25	(0,0,0)
8	.241209	.241207	.240250	0.242423	7	24	(0,0,0)
9	.253944	.253947	.259379	0.284702	0	30	(0,0,1)
10	.255012	.255014	.260476	0.287056	1	30	(0,0,1)
11	.264490	.264492	.269912	0.294118	2	29	(0,0,1)
12	.275801	.275803	.275077	0.278259	8	23	(0,0,0)
13	.276284	.276281	.281334	0.305887	3	28	(0,0,1)
14	.285991	.285990	.296508	0.318344	0	30	(0,1,0)
15	.287061	.287061	.297621	0.320773	1	30	(0,1,0)

[a] The ro-vibrational ground-state energy was calculated at −2.015861 eV relative to the dissociation limit of $H + O_2$, which is referred to as the zero energy point. All energy units are in eV. For these low bound states, quantum numbers (K_a,K_c) and (ν_1,ν_2,ν_3) are used to label the energy levels.

TABLE 2: Selected Low Bound-State Energies for $J = 30$ and Odd Spectroscopic Symmetry from DS/LSFD, LHFD, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.129246	.129247	0.127746	1	29	(0,0,0)
2	.134702	.134703	0.134914	2	28	(0,0,0)
3	.146814	.146815	0.146859	3	27	(0,0,0)
4	.163395	.163395	0.163583	4	26	(0,0,0)
5	.184703	.184702	0.185085	5	25	(0,0,0)
6	.210660	.210659	0.211365	6	24	(0,0,0)
7	.241209	.241207	0.242423	7	23	(0,0,0)
8	.258503	.258505	0.287056	1	29	(0,0,1)
9	.263879	.263881	0.294118	2	28	(0,0,1)
10	.275937	.275832	0.278259	8	22	(0,0,0)
11	.276284	.276281	0.305887	3	27	(0,0,1)
12	.290950	.290950	0.320773	1	29	(0,1,0)

[a] Other symbols are the same as those in Table 1.

TABLE 3: Selected Low Bound-State Energies for $J = 40$ and Even Spectroscopic Symmetry from DS/LSFD, LHFD, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.218531	.218532	0.221060	0	40	(0,0,0)
2	.219106	.219127	0.223449	1	40	(0,0,0)
3	.231164	.231166	0.230617	2	39	(0,0,0)
4	.241808	.241810	0.242562	3	38	(0,0,0)
5	.258330	.258331	0.259286	4	37	(0,0,0)
6	.279508	.279508	0.280788	5	36	(0,0,0)
7	.305336	.305335	0.307068	6	35	(0,0,0)
8	.335742	.335740	0.338126	7	34	(0,0,0)
9	.345684	.345687	0.401214	0	40	(0,0,1)
10	.346266	.346269	0.403568	1	40	(0,0,1)
11	.358167	.358170	0.410630	2	39	(0,0,1)
12	.368656	.368658	0.373962	8	33	(0,0,0)
13	.370658	.370656	0.422399	3	38	(0,0,1)
14	.380266	.380267	0.438677	0	40	(0,1,0)
15	.380826	.380826	0.441106	1	40	(0,1,0)

[a] Other symbols are the same as those in Table 1.

TABLE 4: Selected Low Bound-State Energies for $J = 40$ and Odd Spectroscopic Symmetry from DS/LSFD, LHFD, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.225158	.225160	0.223449	1	39	(0,0,0)
2	.229505	.229452	0.230617	2	38	(0,0,0)
3	.241961	.241962	0.242562	3	37	(0,0,0)
4	.258325	.258326	0.259286	4	36	(0,0,0)
5	.279508	.279508	0.280788	5	35	(0,0,0)
6	.305336	.305335	0.307068	6	34	(0,0,0)
7	.335742	.335741	0.338126	7	33	(0,0,0)
8	.352246	.352249	0.403568	1	39	(0,0,1)
9	.356469	.356471	0.410630	2	38	(0,0,1)
10	.368807	.368810	0.373962	8	32	(0,0,0)
11	.370658	.370656	0.422399	3	37	(0,0,1)
12	.384935	.384937	0.441106	1	39	(0,1,0)

[a] Other symbols are the same as those in Table 1.

PODVR for the *R* coordinate. However, for consistency we will still use the standard PODVR although it may not be the most efficient and accurate choice.

In our calculations, the Chebyshev or Lanczos propagations and FD analysis are separated completely. Although parallel computations are employed only in the propagation step, the FD analyses are performed using conventional nonparallel architectures. Because of the communications and loading balance issues mentioned above, the parallel computing model does not scale ideally with $(J + 1)$ for even spectroscopic symmetry or J for odd spectroscopic symmetry. However, one can achieve wall clock times (e.g., for even symmetry $J = 30$ HO_2 case) that are within about a factor of 5 of $J = 0$ calculations (for the same iteration numbers). For nonparallel computing, the wall clock times will approximately be a factor of 31 of $J = 0$ calculations. We note furthermore that in our calculations this scaling was achieved using just 8 cpus.

3.2. Bound-State Energies. We have employed both methods described above, that is, the real Chebyshev LSFD method incorporating the doubling scheme and the LHFD method, to compute the bound-state energies for two chosen energy windows at $J = 30$, 40, 50 for both spectroscopic symmetries. The first energy window is for the lowest bound-state energies from −0.08 to 0.92 eV. Here the zero on the energy scale refers to the ground-state energy of HO_2 for $J = 0$, which is −2.015861 eV relative to the $H + O_2$ dissociation limit. This energy window is relatively easy to converge, and 100 000 Chebyshev iterations are sufficient to converge all of the bound states within the window. In Tables 1−6 we have listed the selected lowest bound-state energies from both even and odd spectroscopic symmetry calculations for comparison. In these tables, the second and third columns represent the exact quantum mechanical results from real Chebyshev and Lanczos methods, respectively. Inspection of the energies shows that the agreement between them is quite satisfactory and for most of the energies 5−6 digits of relative accuracy have been achieved. For the low-lying bound states of the $J = 30$ (even symmetry) case, we can also compare our calculations with Bunker et al.'s variational results[4,5] (also from private communications). Note that the units in Bunker et al.'s results have been changed from cm^{-1} to eV to facilitate the comparison. Given that different potential energy surfaces have been employed in this work and in Bunker et al.'s work, the agreements between them on the whole are still satisfactory, especially for the lowest part of the spectrum. Here we need to mention that DMBE IV PES tends to predict lower vibrational energy levels than the experimental results, see, for example, ref 67. Also, in Bunker et al.'s work the Renner effect and well spin−orbit coupling have been included, and in our comparison only the energy levels from their $J = 30 + {}^{1}/_{2}$ calculations are considered.

To test the *J* shifting and helicity-conserving approximations for such high *J* values, we have performed the *J*-shifting approximation calculations using Bowman et al.'s adiabatic rotation method[86] for the lowest bound-state energies (*J*-shifting

TABLE 5: Selected Low Bound-State Energies for $J = 50$ and Even Spectroscopic Symmetry from DS/LSFD, LHFD, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.337633	.337636	0.343722	0	50	(0,0,0)
2	.337923	.337925	0.346111	1	50	(0,0,0)
3	.353452	.353455	0.353278	2	49	(0,0,0)
4	.362818	.362821	0.365223	3	48	(0,0,0)
5	.379279	.379281	0.381947	4	47	(0,0,0)
6	.400257	.400258	0.403449	5	46	(0,0,0)
7	.425905	.425906	0.429729	6	45	(0,0,0)
8	.456121	.456120	0.460787	7	44	(0,0,0)
9	.462009	.462013	0.550546	0	50	(0,0,1)
10	.462292	.462296	0.552900	1	50	(0,0,1)
11	.477640	.477644	0.559962	2	49	(0,0,1)
12	.486861	.486864	0.496624	8	43	(0,0,0)
13	.490829	.490828	0.571732	3	48	(0,0,1)
14	.499818	.499819	0.592906	0	50	(0,1,0)
15	.500070	.500071	0.595335	1	50	(0,1,0)

[a] Other symbols are the same as those in Table 1.

TABLE 6: Selected Low Bound-State Energies for $J = 50$ and Odd Spectroscopic Symmetry from DS/LSFD, LHFD, and *J*-Shifting Approximation[a]

n	DS/LSFD	LHFD	J-shifting	K_a	K_c	(ν_1,ν_2,ν_3)
1	.346874	.346877	0.346111	1	49	(0,0,0)
2	.349929	.349932	0.353278	2	48	(0,0,0)
3	.363344	.363347	0.365223	3	47	(0,0,0)
4	.379251	.379252	0.381947	4	46	(0,0,0)
5	.400258	.400259	0.403449	5	45	(0,0,0)
6	.425905	.425906	0.429729	6	44	(0,0,0)
7	.456121	.456121	0.460787	7	43	(0,0,0)
8	.471153	.471157	0.552900	1	49	(0,0,1)
9	.474154	.474158	0.559962	2	48	(0,0,1)
10	.487383	.487386	0.496624	8	42	(0,0,0)
11	.490829	.490828	0.571732	3	47	(0,0,1)
12	.503052	.503055	0.595335	1	49	(0,1,0)

[a] Other symbols are the same as those in Table 1.

and adiabatic rotation approximations are very similar in spirit, and in this paper we have not distinguished them in the discussions). Rotational constants *A*, *B*, and *C* used in this work are taken from the experimental results of Burkholder et al.,[87] which are (20.3565236, 1.1180340, and 1.05631924) for the (0,0,0) band, (20.309223, 1.0741278, and 1.573005) for the (0,0,1) band and (20.957744, 1.0832341, and 1.650704) for the (0,1,0) band (unit in cm^{-1}). For these lowest bound states, a spectroscopic assignment has also been made (see the last three columns). From Tables 1−6 we can see that for the first two lowest energy levels with $K_a = 0$ and 1 in (0,0,0) band, because of their closeness in energy, the mixing of different Ω components of the wave function for $J > 0$ is apparent, and *J*-shifting results are not very close to the quantum results. However, for the following six energy levels with $K_a = 2-7$ in the (0,0,0) band, *J*-shifting results are very close to exact quantum results. For these energy levels, the *J*-shifting approximation is indeed very good, given that the vibrational energy levels from DMBE IV PES are normally lower than the experimental results and that in *J*-shifting approximation we have used experimental rotational constants *A*, *B*, and *C* in this work. For the following energy levels, because of more serious mixing in different band levels, that is, in (0,0,0), (0,0,1) and (01,0), *J*-shifting approximation becomes less accurate in predicting the ro-vibrational energy levels. We note that even in this range of mixing energy levels *J*-shifting still predicts much better results for the (0,0,0) band than for the other two bands, possibly because of more accurate rotational constants *A*, *B*, and *C* or less serious mixing for this band.

Another approximation used widely in dynamical calculations is the so-called helicity-conserving approximation.[88,89] In the helicity-conserving (HC) approximation (also known as centrifugal sudden approximation), the Coriolis coupling blocks, $\hat{H}_{\Omega,\Omega\pm1}$, in eq 3 are simply ignored and the diagonal block, $\hat{H}_{\Omega,\Omega}$, in eq 2 can be solved independently for each Ω at a fixed *J* value. A common characteristic in these different levels of approximations is whether a good quantum number, Ω , exists, and in this paper we do not perform helicity-conserving calculations explicitly, instead we will make a relatively easy comparison of the energy levels with the same K_a but from different spectroscopic symmetries; for example, Table 1 with Table 2, Table 3 with Table 4, and Table 5 with Table 6, to see whether Ω is a good quantum number. Thus, we can judge whether the helicity-conserving approximation is a good approximation. If the calculated energies from even and odd symmetries are nearly the same for the same Ω component, then Ω is a good quantum number. This is because near degeneracy exists for the same Ω components from both symmetries. Therefore, helicity-conserving calculations or even much simpler adiabatic rotation approximations should be accurate, which will save quite a lot of computational time. By such a comparison of the corresponding energy levels, we can see that whenever the energy levels become close, the mixing of different Ω components is more serious, and the differences of the corresponding energy levels become large. For example, for the first two lowest energy levels with $K_a = 0$ and 1 in each (ν_1,ν_2,ν_3) band, because of their closeness in energy, the mixing of these two Ω components is more severe, and the differences of the corresponding energy levels become large. Indeed, through comparison of the energy levels with the same K_a but from different spectroscopic symmetries, we can judge whether Ω is a good quantum number and thus determine whether helicity-conserving or even the much simpler adiabatic rotation approximation are good approximations, that is, if the calculated energies from even and odd symmetries are nearly the same for the same Ω component, then Ω is a good quantum number. Unfortunately, for the HO_2 system this is not true for most bound-state levels, in particular for high *J* values as discussed in this paper. This indicates that for the HO_2 system the Coriolis coupling is very important and various approximations might cause inaccuracies; thus, exact quantum mechanical calculations are needed. Also, it is interesting that the results of these approximations cannot, in and of themselves, tell us whether the approximations are valid or not; such analysis relies on either accurate quantum mechanical calculations or experimental results.

The second energy window we have chosen is close to and above the dissociation threshold from 2.0958 to 2.1758 eV. The computational demands are progressively greater as one moves up into denser regions of the spectrum. In the calculations reported in this paper, we have used the largest Chebyshev iterations of more than 1 000 000 for even symmetry to converge these high-lying bound states. We believe that the iteration number used in this paper is one of the largest published, and interestingly the damped Chebyshev recursion proves to be very stable. In tables 7−9, we have listed selected 60 high-lying bound states for even symmetry of $J = 30$, 40, and 50 from DS/LSFD calculations. For the high-lying bound states, we have failed to assign them unambiguously (indeed even for the $J = 0$ case, one cannot make the assignments for the high-lying bound states of the HO_2 system because of its essentially chaotic characteristic). For example, we have analyzed the high-lying bound-state energies near the dissociation threshold from $J =$

TABLE 7: Selected High-Lying Bound-State Energies from DS/LSFD Calculations for $J = 30$ and Even Spectroscopic Symmetry[a]

n	E_n	*n*	E_n
1	2.097479	31	2.104023
2	2.097618	32	2.104259
3	2.097808	33	2.104390
4	2.098177	34	2.104621
5	2.098459	35	2.104771
6	2.098578	36	2.105079
7	2.098621	37	2.105193
8	2.098820	38	2.105440
9	2.099273	39	2.105529
10	2.099590	40	2.105618
11	2.099644	41	2.105866
12	2.099652	42	2.106084
13	2.100109	43	2.106178
14	2.100455	44	2.106442
15	2.100716	45	2.106813
16	2.100817	46	2.106981
17	2.101054	47	2.107115
18	2.101105	48	2.107307
19	2.101448	49	2.107594
20	2.101639	50	2.107771
21	2.101846	51	2.108062
22	2.102029	52	2.108186
23	2.102114	53	2.108259
24	2.102455	54	2.108442
25	2.102652	55	2.108678
26	2.102863	56	2.108882
27	2.103016	57	2.108983
28	2.103259	58	2.109160
29	2.103532	59	2.109577
30	2.103734	60	2.109759

[a] The ro-vibrational ground-state energy was calculated at −2.015861 eV relative to the dissociation limit of $H + O_2$, which is referred to as the zero energy point. All energy units are in eV.

TABLE 8: Selected High-Lying Bound-State Energies from DS/LSFD Calculations for $J = 40$ and Even Spectroscopic Symmetry[a]

n	E_n	*n*	E_n
1	2.097620	31	2.104973
2	2.097828	32	2.105265
3	2.098278	33	2.105369
4	2.098372	34	2.105674
5	2.098522	35	2.106027
6	2.098745	36	2.106264
7	2.098940	37	2.106496
8	2.099152	38	2.106748
9	2.099396	39	2.107273
10	2.099708	40	2.107407
11	2.099916	41	2.107501
12	2.100081	42	2.107845
13	2.100303	43	2.108027
14	2.100472	44	2.108506
15	2.100798	45	2.108627
16	2.101049	46	2.108783
17	2.101248	47	2.108853
18	2.101565	48	2.109204
19	2.101654	49	2.109601
20	2.102025	50	2.109859
21	2.102200	51	2.110198
22	2.102340	52	2.110376
23	2.102825	53	2.110858
24	2.103106	54	2.110894
25	2.103567	55	2.111140
26	2.103712	56	2.111267
27	2.104019	57	2.111459
28	2.104398	58	2.111635
29	2.104651	59	2.111898
30	2.104860	60	2.112042

[a] Other symbols are the same as those in Table 7.

TABLE 9: Selected High-Lying Bound-State Energies from DS/LSFD Calculations for $J = 50$ and Even Spectroscopic Symmetry[a]

n	E_n	*n*	E_n
1	2.095940	31	2.103903
2	2.096289	32	2.104196
3	2.096725	33	2.104238
4	2.097112	34	2.104542
5	2.097477	35	2.104610
6	2.097537	36	2.104802
7	2.097967	37	2.105254
8	2.098137	38	2.105771
9	2.098375	39	2.106014
10	2.098567	40	2.106200
11	2.098758	41	2.106492
12	2.098945	42	2.106592
13	2.099091	43	2.106832
14	2.099165	44	2.106979
15	2.099851	45	2.107098
16	2.099960	46	2.107309
17	2.100142	47	2.107520
18	2.100804	48	2.107862
19	2.101049	49	2.108247
20	2.101120	50	2.108479
21	2.101236	51	2.108788
22	2.101404	52	2.109068
23	2.101670	53	2.109301
24	2.101739	54	2.109648
25	2.102167	55	2.109788
26	2.102411	56	2.109908
27	2.102725	57	2.110256
28	2.103004	58	2.110365
29	2.103294	59	2.110621
30	2.103631	60	2.110859

[a] Other symbols are the same as those in Table 7.

30 calculations for both even and odd spectroscopic symmetries, respectively (the results for the high-lying bound-state energies for odd symmetry are not shown here, and they can be obtained from the authors upon request). Although only several of them can be assigned tentatively, most of them cannot be assigned with confidence. This indicates that the mixing of different Ω components is so strong that Ω is no longer a good quantum number even qualitatively. Of course, the difficulties in assignment also arise from the fact that the spacings between these high-lying bound states are becoming smaller and smaller. For this system, it seems that HC calculations or adiabatic rotation approximations can give reasonably accurate results only for some low bound-state energies. This observation is consistent with the previously reported $J > 0$ total reaction probability calculations for this system, which show that for HO_2 the Coriolis coupling is important and cannot be ignored.[90] Interestingly, this situation is in contrast to the H_2O and HOCl system, for which HC or AR is a good approximation.[48,91,92]

4. Conclusions

In this paper the doubling scheme/low storage filter diagonalization (DS/LSFD) method as well as the Lanczos homogeneous filter diagonalization (LHFD) method have been applied to the very challenging case of HO_2 with total angular momentum $J = 30$, 40, and 50 to compute low- as well as high-lying bound state energies. Both methods have proved stable over very large numbers of iterations and are capable of computing the entire spectrum from a single recursion. Regarding the relative efficiencies, the two iterative methods are roughly comparable, with the DS/LSFD method being marginally favored. For the low-lying bound states, the results from the DS/LSFD and LHFD methods are in good agreement and they are in general agreement with the variational results reported previously for the $J = 30$ even-symmetry case. Using these quantum results, we have tested the widely used approximate *J*-shifting and helicity-conserving methods for such high *J* values for the HO_2 system. The results indicate that whenever the energy levels become close the mixing of different Ω components of the wave function is more serious and the predictions from *J*-shifting or helicity-conversing approximations will be less reliable. For high-lying bound states, unambiguous assignment becomes impossible becasue of stronger mixing as well as the closeness of the energy levels. For the HO_2 system, the Coriolis coupling is very important and Ω is no longer a good quantum number such that exact quantum mechanical calculations are needed. Such rigorous quantum calculations have only recently become possible through both the parallel computing strategy and the development of more efficient methodology.

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