(*J. Chem. Phys.* **141**, 244114 (2014))

A complex guided spectral transform Lanczos method for studying quantum resonance states

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(January 6, 2015)

Abstract

A complex guided spectral transform Lanczos (cGSTL) algorithm is proposed to compute both bound and resonance states including energies, widths and wavefunctions. The algorithm comprises of two layers of complex-symmetric Lanczos iterations. A short inner layer iteration produces a set of complex formally orthogonal Lanczos (cFOL) polynomials. They are used to span the guided spectral transform function determined by a retarded Green operator. An outer layer iteration is then carried out with the transform function to compute the eigen-pairs of the system. The guided spectral transform function is designed to have the same wavefunctions as the eigenstates of the original Hamiltonian in the spectral range of interest. Therefore the energies and/or widths of bound or resonance states can be easily computed with their wavefunctions or by using a root-searching method from the guided spectral transform surface. The new cGSTL algorithm is applied to bound and resonance states of HO₂, and compared to previous calculations.

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1 Introduction

Since Paige and Saunders¹ discovered that spurious eigenstates (also called ghosts) appearing in the standard Lanczos iterative diagonalization² did not preclude the calculation of the true eigenstates in 1975,^{3,4} the Lanczos algorithm² has been widely used in many fields^{5,6} including molecular spectroscopy⁶⁻¹⁵ and chemical dynamics.¹⁶⁻²³ The Lanczos method has many merits, e.g., see the reviews^{6,8,22,24} and references therein. For instance, it requires only the action of matrix (or quantum Hamiltonian) on Lanczos vectors, which is very suitable for large sparse matrices and parallel computing. In chemical physics, the Hamiltonian-vector products are usually evaluated on-the-fly without explicitly constructing Hamiltonian matrices. Thus the requirement of core memory is roughly defined by the size of two Lanczos vectors if only eigenvalues are wanted.

The standard Lanczos algorithm is also very efficient to compute extreme and widely spaced eigenstates but becomes rather slow to converge interior states in dense spectrum regions where eigenvalues are clustered with small spacings. Techniques such as the restarting approach²⁵⁻³⁰ and the projection or filter diagonalization methods^{7,12,31-40} have been developed in order to speed up the computation of those interior eigenstates. In particular, Ericsson and Ruhe⁴¹ proposed an excellent spectral transform technique in which they used a shifted and inverted matrix instead of the matrix itself to carry out the Lanczos iterations. As a result, the states near the shift value are calculated quickly as in this region the transformed matrix has a strongly dilated spectrum. Indeed, the spectral transform Lanczos (STL) method has fully taken the advantage of the Lanczos method. The powerful spectral transform technique has then been explored by several groups including us^{12,42-51} in chemical physics. The most used functions $f(\hat{H})$ are the Green function $(\hat{H} - E_0)^{-1}$,^{12,42,49,50,52} the exponential function $\exp[-\alpha(\hat{H} - E_0)]$,^{43,48,53} the Gaussian $\exp[-\alpha(\hat{H} - E_0)^2]$ ⁵¹ and its derivative $(\hat{H} - E_0) \exp[-\alpha(\hat{H} - E_0)^2]$,⁴⁴ and the hyperbolic tangent $\tanh[\alpha(\hat{H} - E_0)]$.⁴⁵ Nevertheless, the STL method has not been widely applied

for large systems. This is largely because it is difficult and computationally expensive to perform the actions of the spectral transform $f(\hat{H})$ on Lanczos vectors^{44,47,48} owing to the nonlinearity of $f(\hat{H})$.

In order to avoid this difficulty, we have recently developed an efficient guided spectrum transform Lanczos (GSTL) method.^{45,54} The GSTL method uses a mimic function $F(\hat{H})$ of an analytic function $f(\hat{H})$ as mentioned above. Here $F(\hat{H})$ is a low order polynomial obtained by truncating the accurate expansion of $f(\hat{H})$ in orthogonal polynomials. The efficiency of the GSTL algorithm also relies on the fact that the action of $F(\hat{H})$ -vectors can be efficiently done via the recurrence polynomial-vector products. The GSTL method is problem-independent. It has been widely used in high dimensional quantum reactive scattering (e.g. see Refs.[21,22] and references therein) and molecular spectroscopy^{22,49,55} calculations. By using the GSTL method, we have developed a two-layer Lanczos algorithm^{56,57} that is capable of solving the eigenvalue problem of polyatomic systems up to six atoms without any dynamics approximation.⁴⁹ It also makes possible the routine calculation of vibrational energies of four- and five-atom molecules,^{13,55} once a global potential energy surface of molecule is provided.

Although the STL/GSTL methods have been successfully implemented with Hermitian matrices or operators, their application for non-Hermitian complex matrices is still rather limited. In chemical physics, one often needs to study resonance states (similar to bound states but having complex eigenvalues). They are usually computed by using an extended Hamiltonian,

$$\hat{H} = \hat{H}_s - iW, \quad (1)$$

in a square integrable (L^2) basis set. Here $\hat{H}_s$ is the system Hamiltonian while $-iW$ refers to a negative imaginary potential (NIP)^{58,59} to impose boundary conditions. Obviously, its Hamiltonian matrix is no longer Hermitian but complex symmetric. It gives complex eigenvalues as $z_n = E_n - i\Gamma_n/2$ in which E_n and Γ_n are the energies and widths, re-

spectively. Nowadays, the complex symmetric Lanczos algorithm^{46,52,60–64} is often used to solve the eigen-equation of Eq. (1) although the algorithm may suffer from the numerical instability problem for long iterations.^{5,59} Therefore, the algorithm is inefficient to study resonances in dense regions, for example, those resonances that appear above a deep potential well, as in molecules HO₂, NO₂ and HOCO etc. A combined filter diagonalization and Lanczos iteration approach^{7,40,63,65} has been proposed to improve the convergence of calculations. On the other hand, if one is interested only in resonance energies and widths, there are several efficient algorithms based on the real (damped) Chebyshev propagation methods^{33–35,66–71} in addition to the Lanczos,^{7,63,73} Newton,^{74–77} and Faber^{20,78} polynomial expansions. Leforestier and co-workers⁵² have proposed a spectral transform Lanczos method by using an LU decomposition of complex scaled Hamiltonian. However, those low-storage methods are inferior to calculating the wavefunctions of resonance states since a restarting iteration has to be done for extracting wavefunctions. Therefore, it is still challenging to compute resonance wavefunctions beyond resonance energies and widths, especially, for those long-lived resonances in large systems.

In this work, we present a direct extension of our real guided spectral transform Lanczos method⁵⁴ to incorporate complex symmetric matrices and thereby enable the calculations of resonance states including energies, widths and wavefunctions. The spectral transform function is produced with the guidance of the retarded Green operator $G^+(E)$, and is expanded in a series of complex formally orthogonal Lanczos (cFOL) polynomials. The cFOL polynomials are used in order to avoid the numerical instability of classical orthogonal polynomial expansion that is normally utilized in real algorithms. In Sec. 2 we will describe the extended version, which we name the complex guided spectral transform Lanczos (cGSTL) method. Numerical application and results for computing both the bound and resonance states of HO₂ are discussed in Sec. 3. Finally a short summary is given in Sec. 4.

2 The complex guided spectral transform Lanczos method

Similar to the real Lanczos algorithm, the complex-symmetric Lanczos recursion can be written as^{46, 52, 60–64}

$$\beta_{j+1}|\psi_{j+1}\rangle = \hat{H}|\psi_j\rangle - \alpha_j|\psi_j\rangle - \beta_j|\psi_{j-1}\rangle, \quad (2)$$

where $\hat{H}$ is the extended Hamiltonian in Eq. (1). α_j and β_j are the complex mean value and residual of the j^{th} vector respectively. They are defined as

$$\alpha_j = (\psi_j|\hat{H}|\psi_j), \quad \beta_{j+1} = (\psi_{j+1}|\hat{H}|\psi_j) \quad (3)$$

with

$$\beta_1 = 0, \quad |\psi_0\rangle = 0. \quad (4)$$

Basically, the Lanczos recursion reduces the original Hamiltonian matrix to a symmetric tridiagonal form

$$\mathbf{T}_K = \begin{bmatrix} \alpha_1 & \beta_2 & & \\ \beta_2 & \alpha_2 & \beta_3 & 0 \\ & \beta_3 & \ddots & \ddots \\ & 0 & \ddots & \ddots & \beta_K \\ & & & \beta_K & \alpha_K \end{bmatrix} \quad (5)$$

in the K^{th} order subspace $\mathbf{V}_K = \{|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_K\rangle\}$ with the orthonormal conditions⁶²

$$(\psi_i|\psi_j) = \delta_{ij}, \quad (6)$$

where $'(\dots|\dots)'$ refers to a c -product (i.e., no complex-conjugation in contrast to normal Hermitian cases). In matrix form Eq. (2) can be expressed as

$$\hat{H}\mathbf{V}_K = \mathbf{V}_{K+1}\mathbf{T}_K = \mathbf{V}_K\mathbf{T}_K + \beta_{K+1}\psi_{K+1}e_K^T. \quad (7)$$

Here $'T'$ stands for transpose only, and e_j being an unit vector in the j^{th} dimension.

Following our real GSTL algorithm,^{45, 49, 54} the complex guided spectral transform Lanczos (cGSTL) algorithm is given by

$$\beta_{j+1}|\psi_{j+1}\rangle = F(\hat{H})|\psi_j\rangle - \alpha_j|\psi_j\rangle - \beta_j|\psi_{j-1}\rangle, \quad (8)$$

or in the matrix form

$$F(\hat{H})\mathbf{V}_K = \mathbf{V}_{K+1}\mathbf{T}_K = \mathbf{V}_K\mathbf{T}_K + \beta_{K+1}\psi_{K+1}e_K^T, \quad (9)$$

where $F(\hat{H})$ is a guided spectral transform function of $\hat{H}$. The difference to Eq. (7) is that instead of using the Hamiltonian directly in the recursion a function of the Hamiltonian, $F(\hat{H})$, is used. Again $F(\hat{H})$ will be expanded in a set of complex orthogonal polynomial functions.

As usual, we aim at the calculation of the lowest lying resonance states of $\hat{H}$ as well as the bound states below them. Even so, the number of states can be large for molecules with deep potential wells. For this purpose a good $F(\hat{H})$ should have a strongly dilated spectrum at low energies and widths near zero, and be a monotonic function in the spectral range of interest. As a result, the eigenstates of $F(\hat{H})$ in the dilated spectrum can be computed quickly by the Lanczos method, and the calculated states can uniquely match with those of $\hat{H}$. Our previous studies have shown that the exponential⁵⁴ and the hyperbolic tangent⁴⁵ functions are good choices. Their transform functions can be robustly expanded in a series of classical orthogonal polynomial functions⁷⁹ such as Chebyshev or Legendre in the case of Hermitian Hamiltonian. Unfortunately, the same approach can not be applied for constructing $F(\hat{H})$ with a complex non-Hermitian Hamiltonian owing to the numerical instability and/or the strongly oscillating behavior in the imaginary direction. It is well known that the standard Chebyshev recursion is unstable for a complex Hamiltonian^{76,78} despite being the best one for a Hermitian operator. Alternatively, the Newton⁷⁴⁻⁷⁷ and Faber^{20,78} polynomials have often been employed for complex Hamiltonian in quantum dynamics calculations. However, it is noticed that both polynomial expansions are not satisfied to represent the spectral transform function. This is because the spectrum is hardly dilated along the imaginary direction near zero.

Eventually, it is found that the complex guided spectral transform function $F(\hat{H})$ can be expressed in a series of complex formally orthogonal Lanczos (cFOL) polynomi-

als $(\mathcal{L}_k(\hat{H}))$,⁸⁰ i.e.

$$F(\hat{H}) = \sum_{k=1}^{L_C} A_k(E_{ref}) \mathcal{L}_k(\hat{H}). \quad (10)$$

Similar to the standard Lanczos recurrence in Eq. (2), the cFOL polynomials can be obtained using the recurrence

$$\beta_{k+1} \mathcal{L}_{k+1} = \hat{H} \mathcal{L}_k - \alpha_k \mathcal{L}_k - \beta_k \mathcal{L}_{k-1}, \quad (11)$$

with

$$\mathcal{L}_0(\hat{H}) = 0 \quad \text{and} \quad \mathcal{L}_1(\hat{H}) = 1.$$

By using the property of the Lanczos polynomials

$$(E' | \mathcal{L}(\hat{H}) | E) = \mathcal{L}(E) \delta_{EE'}, \quad (12)$$

one can write the transformed spectral surface as

$$F(E) = \sum_{k=1}^{L_C} A_k(E_{ref}) \mathcal{L}_k(E), \quad (13)$$

where E is a complex variable.

In Eq. (10) the expansion coefficients $\mathbf{A}_k^T = \{A_1(E_{ref}), A_2(E_{ref}), \dots, A_k(E_{ref})\}$ are determined by the guidance of the retarded Green function ($G^+(E_{ref}) = (\hat{H} - E_{ref})^{-1}$) with a given reference pivot (real or complex). Then they are obtained by solving the linear equation

$$\mathbf{L}_k \mathbf{L}_k^T \mathbf{A}_k = ((\mathbf{T}_k - E_{ref} \mathbf{I})^2 + \beta_{k+1}^2 e_k e_k^T) \mathbf{A}_k = (\mathbf{T}_k - E_{ref} \mathbf{I}) e_1 \quad (14)$$

that is an extended version of the minimal residual (MINRES) equation.^{1,12} Here the lower tri-band matrix $\mathbf{L}_k$ is defined for the shift E_{ref} as

$$\mathbf{L}_k = \begin{bmatrix} \gamma_1 & & & & \\ \delta_2 & \gamma_2 & & & \\ \epsilon_3 & \delta_3 & \ddots & 0 & \\ & \epsilon_4 & \ddots & \ddots & \\ 0 & & \ddots & \ddots & \ddots \\ & & & \epsilon_k & \delta_k & \bar{\gamma}_k \end{bmatrix}. \quad (15)$$

The complex elements γ_i , δ_i and ϵ_i are calculated from the Lanczos coefficients α_i and β_i in Eq. (2) using a LQ factorization method.^{1,5} The Lanczos coefficients are first calculated with any initial random vector.

Since we are interested in obtaining a desired spectral transform function $F(\hat{H})$ rather than in converging the retarded Green function, a low order (L_C) expansion in Eq. (10) is always used. The value L_C is selected by the condition $|A_{L_C}(E_{ref})| < 0.01$ in which L_C is the minimum subspace $k = L_C$ in Eq. (14). The criterion (0.01) is the same as that optimized in the real GSTL method.^{45,54} It is worthwhile to mention that, unlike the Chebyshev or other classical orthogonal polynomial expansions, the MINRES algorithm optimizes the expansion coefficients with respect to the subspace size k too. Therefore, it is not necessary that the l^{th} coefficient $|A_l|$ will always decay with increasing k . In other words, the truncation method^{45,54} starting with a given large subspace size k is not an optimal way to determine L_C . This is why we propose the opposite procedure beginning at a small subspace. This approach has been numerically verified.

Furthermore, the complex quasi-MINRES method (QMR) was used by Yu and Smith⁶³ for the calculation of resonance energies and widths, in which the Green operator is utilized as a filter operator. In order to get a nearly energy-resolved filter, a long Lanczos recursion has to be carried out for computing approximate filter states. In contrast, the cGSTL method uses the Green operator as a spectral transform reference rather than a filter operator. Here, other crucial difference is that the QMRFD method does the standard Lanczos iterations with Hamiltonian $\hat{H}$ whereas the cGSTL method performs the iterations with a spectral transform function of $\hat{H}$.

Now we can summarize the cGSTL calculations as following steps:

- (i) Select an initial Lanczos vector, and run a short Lanczos iteration in Eq. (2) to obtain a set of Lanczos coefficients (α_j, β_j) .
- (ii) Give a reference E_{ref} , and determine the order L_C and expansion coefficients A_k in

$F(\hat{H})$ by solving the MINRES equation (14) based on the Lanczos coefficients.

(iii) Select another initial Lanczos vector, and perform the spectral transform Lanczos iterations in Eq. (8) using the pre-defined function $F(\hat{H})$ until converge N -wanted bound/resonance states.

(iv) Calculate the eigenvalues ($F(E_n)$) and eigenvectors ($|\psi_n\rangle$) of $F(\hat{H})$, and find the eigenvalues (E_n) of $\hat{H}$ either using a root-searching method from $F(E_n)$ via Eq. (13) or directly computing with $E_n = \langle \psi_n | \hat{H} | \psi_n \rangle$ as both $\hat{H}$ and $F(\hat{H})$ share the same eigenvectors in this spectral region.

Actually, the cGSTL algorithm in step (iii) involves two layers of complex-symmetric Lanczos iterations. A short inner layer iteration (L_C) is repeated, using the coefficients (α_j, β_j) in step (i), to yield the spanning cFOL polynomials for the $F(\hat{H})$ -vector products. A long outer layer iteration is the one described in Eq. (8). Since L_C is usually small, about ten, the generated cFOL polynomials are orthonormal. In contrast, the orthogonality of the Lanczos vectors in the outer layer will be lost after a few tens of iterations owing to the finite precision of machine. In order to avoid this loss of orthogonality, here, we have applied the partial reorthogonalization procedure of Simon.^{48,81} For more details, the reader can see Ref.[81]. As a result, one can not only avoid the spurious problem but also resolve degenerate states in calculations.

One can notice a few advantages of the cFOL polynomial expansion approach for $F(\hat{H})$. For instance, it is problem-independent. As the expansion coefficients A_k are obtained from the molecule-adapted parameters (i.e., they are calculated using a real Hamiltonian), the order L_C is optimal to the system of interest. A small order will substantially enhance the efficiency of the cGSTL algorithm because the CPU time increases approximately linearly with L_C . In particular, the action of $F(\hat{H})$ on $|\psi_j\rangle$ can be efficiently performed using the three term recurrence of Lanczos polynomials, which is similar to other real classical orthogonal polynomials⁷⁹ such as Chebyshev. Of course, the cFOL polynomials are also

applicable for expanding other operators except for the Green operator.

3 Numerical results and discussion

In this section, we will present an application of the new cGSTL algorithm to calculating the bound states and lowest-lying resonances of the hydroperoxyl radical HO_2 . HO_2 is a benchmark molecule with two equivalent deep potential wells. Its bound and resonance energies and widths have been extensively studied.^{12,63,65,66,68,82,83} As in our previous study,⁶³ we used the Jacobi coordinates $(R_{\text{H-OO}}, R_{\text{OO}}, \theta)$ with zero total angular momentum $J = 0$. Thus the system Hamiltonian is written as

$$\begin{aligned} \hat{H}_s = & -\frac{\hbar^2}{2\mu_{\text{H,OO}}} \frac{1}{R_{\text{H-OO}}} \frac{\partial^2}{\partial R_{\text{H-OO}}^2} R_{\text{H-OO}} - \frac{\hbar^2}{2\mu_{\text{OO}}} \frac{1}{R_{\text{OO}}} \frac{\partial^2}{\partial R_{\text{OO}}^2} R_{\text{OO}} \\ & - \left(\frac{1}{2\mu_{\text{H,OO}} R_{\text{H-OO}}^2} + \frac{1}{2\mu_{\text{OO}} R_{\text{OO}}^2} \right) \frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + V, \end{aligned} \quad (16)$$

where V is the potential energy surface of HO_2 . The DMBE IV surface⁸⁴ is used for numerical test and comparison with other work. At the equilibrium geometry, the potential value is -2.378377 eV relative to the dissociation limit of $\text{H} + \text{O}_2$. In Eq. (1) the absorbing potential is given by⁶³

$$W(R_{\text{H-OO}}) = \frac{V_0}{\cosh^2[(R_{\text{max}} - R_{\text{H-OO}})/\lambda]} \quad (17)$$

with the parameters $V_0 = 2.0 \text{ eV}$, $R_{\text{max}} = 11.0 a_0$, and $\lambda = 0.50 a_0^{-1}$.

The Hamiltonian is represented in a DVR basis set. 110 potential optimized DVR (PODVR) points are used for the $R_{\text{H-OO}}$ coordinate in the range $[0.5, 11.0] a_0$. 50 PODVRs spanning the range $[1.3, 5.0] a_0$ are for R_{OO} . To take account for the odd O-O exchange parity, 43 odd symmetry-adapted Gauss-Legendre pivots are adopted for the θ angle. Furthermore, the direct product DVR basis set is contracted by using a threshold energy of 2.0 eV, which gives a final basis size of 105781. A total 400 lowest-lying states will be computed with a convergence within $1.0 \times 10^{-8} \text{ eV}$.

The normal complex symmetric Lanczos algorithm was first run with 50 iterations with a random initial vector. The obtained Lanczos iteration parameters were then used to determine the expansion coefficients in $F(\hat{H})$ with a reference $E_{ref} = 0.0$ eV in the retarded Green operator. The E_{ref} value was selected to calculate the lowest lying resonance states near the $H + O_2$ dissociation limit in addition to all bound states. According to the criterion (0.01) discussed above, the order of cFOL polynomial expansion is obtained as $L_C = 6$. It is very small, and also implies the efficiency of Green operator filter. The parameters obtained are listed in Table 1. One can see that the absolute values of $|A_k|$ gradually decrease as k increasing. The imaginary parts of A_k are small but noticeable compared to their real parts. This is a general behavior observed.

By using the parameters in Table 1, we have explored the transformed spectral surface that is shown in Fig. 1. The surface does not look like a Green function owing to the short expansion. As desired, the real component of $F(E)$ displays an exponential-like profile along the real energy axis and remains the same property in the imaginary direction. That is, the $F(\hat{H})$ function has substantially dilated the energy spectrum at low energies regardless of widths. Importantly, the imaginary sheet of $F(E)$ also gives wonderful feature that largely dilate the width spectrum monotonically at low energies. At high energies, both the real and imaginary sheets become flat toward zero but having small oscillating waves. Nevertheless, those waves will not affect our calculations as they are well separated from the spectrum at low energies. Indeed, the flat transformation at high energies says that the corresponding transformed spectrum is very dense, in which the states are unwanted.

The lowest 400 states of HO_2 with odd O-O exchange parity have been well converged using 2160 cGSTL iterations. The highest bound states are given in Table 2 while the lowest resonances are listed in Table 3, together with a comparison with previous theoretical results^{63,66,82,83} based on the same potential energy surface. Our results are in excellent agreement with them except for that a few of artificial resonance states are also obtained.

(see discussion below). The cGSTL algorithm demonstrates a better efficiency compared to the order of polynomial iterations in previous studies.^{63,66,82,83} For instance, to converge the same states as in this work, the Chebyshev-based filter diagonalization method of Mandelshtam et al.⁶⁶ needs 40000 real propagations while the QMRSD and QMRFD methods⁶³ require 55000 and 40000 complex iterations respectively. The QMRFD method is also a filter diagonalization method but using the complex Lanczos recurrence. Since the cGSTL algorithm is a nested Lanczos method, its equivalent single-loop iterations are 10800 ($2160 \times (L_C - 1)$ with $L_C = 6$) in complex or 21600 in real. Here a similar contracted basis size is used in the Chebyshev-based FD (130K), QMRFD (106K) and cGSTL (106K) methods. It is also found that the number of cGSTL iterations to converge those eigenstates is not sensitive to the strength V_0 of absorbing potential (within 20 deviations). Here one should notice that the old Chebyshev-based FD method⁶⁶ is not optimal. A better convergence can be achieved by using the improved Chebyshev-based algorithm with multiple optimal damping parameters.⁸⁵ As similar to other filter diagonalization methods,^{7,31,32,35,85} the cGSTL method enables us to compute wavefunctions easily. Compared with those Chebyshev-based methods that calculate the whole energy range equally, the cGSTL algorithm has a strong bias to the dilated spectral region. That is, a single run with the cGSTL algorithm is expected to compute about up to one thousand states efficiently at a time.

The two highest bound states are displayed in Fig. 2. As expected, their wavefunctions are localized above the potential well, and quickly decay to zero at large Jacobi coordinate $R_{\text{H-OO}}$. In contrast, the wavefunction density of a resonance state will spread into the $\text{H} + \text{O}_2$ dissociation channel along the radial Jacobi coordinate because of the nature of scattering states. For HO_2 , two typical resonance states are shown in Fig. 3, where the vanishing densities at the edge of large $R_{\text{H-OO}}$ are due to the absorbing potential $W(R)$ used in the calculations. Here the absorbing potential prevents the reflection of wavefunctions

from the edge, and let resonance states behave correctly in the interaction region. In Fig. 3 the $E_n = 0.099908$ eV state is a normal resonance but the $E_n = 0.103597$ eV resonance is unusual. The latter has large amplitudes in the $\text{H} + \text{O}_2$ dissociation channel. Actually, this kind of states are artificial resonance states³³ as they are not stable with the strength of absorbing potentials. At the trajectory cusp points they would converge to true resonance states.

The eigenvalue trajectories of resonances can be calculated using the perturbation theory with the help of the perturbed Hamiltonian,

$$\hat{H}'(\lambda_s) = \hat{H} + \lambda_s(-iW), \quad (18)$$

with $\lambda_s \geq -1$. By using the eigenstates ψ_n of $\hat{H}$, we have its Hamiltonian matrix elements,

$$\mathbf{H}'_{ij} = z_i \delta_{ij} + \lambda_s [\mathbf{C}^T \mathbf{W}^{cGSTL} \mathbf{C}]_{ij} \quad (19)$$

and

$$\mathbf{W}_{kl}^{cGSTL} = (\psi_k | -iW | \psi_l), \quad (20)$$

where z_i and $\mathbf{C}$ are the eigenvalues and eigenvectors of $\mathbf{H}$. And $\mathbf{W}^{cGSTL}$ is the matrix of the negative imaginary potential in the guided spectral transform Lanczos subspace. This symmetric matrix is calculated only once during the Lanczos propagation. In this example, it has a dimension of 2160. The eigenvalue trajectories are then evaluated by changing the parameter λ_s in the 40 highest eigenstates of $\hat{H}$. A typical trajectory is shown in Fig. 4. These calculations are very fast. Therefore, multiple Lanczos propagations can be avoided.

4 Summary

We have developed a complex guided spectral transform Lanczos (cGSTL) algorithm for studying the bound and resonance states of molecules. By using this method, both complex eigenvalues and eigenvectors (or wavefunctions) can be calculated. The algorithm is

formed by two layers of complex symmetric Lanczos iterations. In particular, we have proposed a numerically robust technique to build up the complex guided spectral transform function $F(\hat{H})$ that is expanded in a series of complex formally orthogonal Lanczos (cFOL) polynomials. The new algorithm has been applied for studying the bound and resonance states of the prototype HO_2 . Calculated energies and widths are in good agreement with previous results. The numerical application shows that the cGSTL method is more efficient compared to other algorithms, and is capable of providing wavefunctions as well as energies and widths. Importantly, the algorithm is problem-independent so that it can be combined with other techniques such as multi-layer basis contraction to get better efficiency.

Acknowledgments

This work was performed at Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. It also used the resource at NERSC.

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Table 1: The Lanczos recurrence coefficients (α_k, β_k) in eV and the expansion parameters $A_k(E_{ref})$ with $E_{ref} = 0.0$ eV.

k	α_k	β_k	A_k
1	(4.88743474, -0.07689197)	...	(0.32064155, 0.01499251)
2	(8.83652709, -0.02763156)	(3.63591360, 0.00007170)	(-0.18217999, -0.01336861)
3	(17.07405668, -0.09132401)	(6.19472456, 0.05132989)	(0.09223438, 0.00901126)
4	(17.04257005, 0.03263378)	(9.73912037, 0.00285816)	(-0.05883206, -0.00590884)
5	(18.33514909, 0.05016775)	(9.14477624, -0.01630337)	(0.02658333, 0.00256294)
6	(16.39878832, 0.15186702)	(9.21863377, -0.05136340)	(-0.00811432, -0.00064216)
7	...	(9.18164233, -0.07287073)	

Table 2: A comparison of computed highest bound states of HO_2 with the total angular momentum $J = 0$ and odd O-O exchange parity, where E_0 is the vibrational ground state while E_n are the energy levels with respect to the asymptote $\text{H} + \text{O}_2$. The energy unit is eV.

MGT ⁶⁶			YS ⁶³	This work
n	$E_n - E_0$	E_n	E_n	E_n
336	2.06234	0.04658	0.04669	0.046693
337	2.06320	0.04744	0.04766	0.047713
338	2.06643	0.05067	0.05102	0.051020
339	2.06854	0.05278	0.05316	0.053161
340	2.07000	0.05424	0.05471	0.054712
341	2.07188	0.05612	0.05629	0.056296
342	2.07277	0.05701	0.05711	0.057109
343	2.07446	0.05870	0.05895	0.058949
344	2.07692	0.06116	0.06166	0.061657
345	2.07722	0.06146	0.06170	0.061709
346	2.08127	0.06551	0.06600	0.066009
347	2.08157	0.06581	0.06642	0.066424
348	2.08224	0.06648	0.06721	0.067211
349	2.08703	0.07127	0.07168	0.071681
350	2.08900	0.07324	0.07354	0.073547
351	2.09103	0.07527	0.07580	0.075804
352	2.09268	0.07692	0.07729	0.077296
353	2.09565	0.07989	0.08017	0.080170
354	2.09649	0.08073	0.08090	0.080904
355	2.09800	0.08224	0.08255	0.082555
356	2.10144	0.08568	0.08614	0.086136
357	2.10607	0.09031	0.09040	0.090407
358	2.10697	0.09121	0.09150	0.091503
359	2.10804	0.09228	0.09263	0.092631
360	2.10997	0.09421	0.09448	0.094480
361	2.11232	0.09656	0.09706	0.097059

Table 3: A comparison of computed energies (E_n) and widths (Γ_n) of the lowest resonance states of HO₂ for $J = 0$ and odd O-O exchange parity. The numbers in parentheses are the power of 10. All units are in eV.

KP ^{82,83}		MGT ⁶⁶		YS ⁶³		This work	
E_n	Γ_n	E_n	Γ_n	E_n	Γ_n	E_n	Γ_n
0.098056	1.841(-4)	-	-	-	-	-	-
0.099152	6.387(-6)	0.099075	2.8(-5)	0.099177	3.454(-5)	0.099189	3.153(-6)
0.099661	6.151(-5)	0.09972	3.2(-5)	0.099896	2.687(-5)	0.099908	1.604(-5)
0.100274	8.227(-4)	-	-	0.100376	5.571(-4)	0.100956	6.184(-4)
0.102036	9.471(-5)	0.10189	8.6(-5)	0.101886	7.214(-5)	0.101907	4.361(-5)
0.103760	1.527(-5)	0.103717	1.56(-5)	0.103758	1.671(-5)	0.103761	1.168(-5)
0.104668	2.334(-5)	0.104622	3.2(-5)	0.104857	6.096(-5)	0.104862	4.399(-5)
0.107208	1.066(-4)	0.106964	7.6(-5)	0.106997	5.051(-5)	0.107005	3.022(-5)
0.110424	1.779(-4)	0.11034	1.14(-4)	0.110754	1.427(-4)	0.110770	5.101(-5)
0.112204	9.403(-4)	0.11214	7.4(-4)	0.112588	3.611(-4)	0.112582	6.896(-4)
0.114299	6.209(-5)	0.11391	1.8(-4)	0.114234	1.020(-4)	0.114264	4.404(-5)
0.115788	6.300(-7)	0.11561	2.6(-7)	0.115654	1.200(-6)	0.115572	5.308(-7)
-	-	0.11872	2.30(-3)	0.117880	3.558(-3)	0.118760	2.717(-3)
0.118964	1.060(-5)	0.11878	1.56(-5)	0.119039	1.254(-5)	0.119037	3.084(-6)
0.120778	3.827(-5)	0.12058	3.6(-5)	0.120751	3.763(-5)	0.120750	4.893(-5)
0.124675	2.491(-5)	0.124484	1.82(-5)	0.124701	1.651(-5)	0.124702	2.224(-5)
0.126862	5.266(-4)	0.12657	4.70(-4)	0.126852	4.663(-4)	0.126583	7.728(-4)
0.127474	1.135(-4)	0.127312	8.44(-5)	0.127592	5.192(-5)	0.127607	7.304(-5)
0.130950	4.885(-5)	0.130690	6.88(-5)	0.130749	5.596(-5)	0.130765	4.204(-5)
0.133196	8.776(-3)	0.132897	2.36(-3)	0.132643	1.359(-3)	0.133164	1.377(-3)
0.135807	1.284(-4)	0.135603	2.20(-4)	0.135814	5.085(-4)	0.135861	2.199(-4)
0.136527	3.816(-4)	0.136566	3.74(-4)	0.136195	3.717(-4)	0.136327	2.939(-4)
0.138706	8.227(-4)	0.13848	7.80(-4)	0.138631	1.253(-3)	0.138645	1.047(-3)
0.141310	5.485(-4)	0.141133	4.76(-4)	0.141486	3.719(-4)	0.141496	4.821(-4)

Figure 1: A plot for the guided spectral transform surface $F(E - E_{ref})$ as a function of energy and resonance width in eV, where its real and imaginary part is shown in the upper and lower panels, respectively.

Figure 2: Wavefunctions for the two highest bound states, $n = 361$ (upper panel) and $n = 360$ (middle panel), with the contour plot of 2D potential energy surface in the Jacobi coordinates (lower panel).

Figure 3: As the same as in Fig. 2 but for two typical resonance states, $E_n = 0.103597$ eV (upper panel) and $E_n = 0.099908$ eV (middle panel).

Figure 4: An eigenvalue trajectory of a typical resonance state obtained by changing the perturbation strength of absorbing potential.

Fig.1

Fig.2

Fig.3

Fig.4