Reduced-Order Modeling, Error Estimation, and the Role of the Start-Vector: The Recursive Residue Generation Method Revisited†

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The recursive residue generation method (RRGM) [Wyatt, R. E. *Adv. Chem. Phys.* **1989**, *73*, 231] is rederived using the formalism of reduced-order modeling [Bai, Z. *Appl. Numerical Math.* **2002**, *43*, 9]. A stopping criteria for the RRGM recursions is proposed, on the basis of an expression for an upper bound to the absolute error [Bai, Z.; Ye, Q. *Electron. Trans. Numerical Anal.* **1998**, *7*, 1]. It is further pointed out that, in general, the start-vector has a negligible effect on the convergence of the RRGM.

I. Introduction

Many problems in chemical physics can be formulated in terms of transition amplitudes between well-defined initial and final states, e.g., in spectroscopy, reactive scattering, and laser−molecule interactions. The recursive residue generation method (RRGM)[1] was introduced by Wyatt and co-workers to be able to compute transition amplitudes, both time-dependent and time-independent, even though the dimension of the underlying Hamiltonian matrix is prohibitively large. The RRGM is based on the observation that by using chemically motivated initial states, or a linear combination thereof, the Lanczos algorithm[2] can be used to compute matrix elements of, e.g., the time-evolution operator or Green's function, without explicit calculation of the eigenstates of the Hamiltonian. It should be mentioned that other groups, e.g., those of Cederbaum[3] and Freed,[4,5] also explored the use of Lanczos method for solving problems in chemical physics at the same time as the RRGM was developed.

The Lanczos method only requires three vectors to be stored and the Hamiltonian matrix only enters in a matrix−vector multiplication, allowing for direct methods. One key component that contributed to the widespread use of the Lanczos method was the possibility to use direct methods for the matrix−vector multiplication, i.e., avoiding the need to explicitly store the full Hamiltonian matrix, computing the matrix−vector product on the fly. Direct methods have been used in electronic structure calculations since the early 1970's.[6] In chemical physics it was the development of pseudo-spectral discretization,[7,8] and specifically the use of the fast Fourier transform for computing the action of the kinetic energy operator,[9−11] that opened up for the use of direct methods, which in turn led to the widespread use of the Lanczos algorithm we see today.

The RRGM has successfully been applied to a number of problems in chemical physics, see, e.g., refs 12−27. The original RRGM formulation considered only transitions between two states but were later extended to compute multiple transition amplitudes[21] with the drawback that several Lanczos propagations are needed. Several attempts have been made to overcome this drawback. Guo and co-workers[28−31] proposed the single Lanczos propagation (SLP) method, in which an arbitrary initial state is used to generate a Lanczos basis from which residues and eigenvalues are computed using a modified QL-algorithm. A similar approach was taken by Smith and co-workers,[32−35] termed the Lanczos subspace method. Karlsson and Holmgren proposed an approach based on solving linear system of equations,[36] and Karlsson[37] advocated for the use of a band-Lanczos method that requires somewhat more memory but includes the initial and final states explicitly in the recursion. Another approach to low-storage computation of transition matrix elements, inspired by the RRGM, is the use of Chebychev polynomials.[38]

To compute matrix elements of very large matrices, computational schemes have also been developed in other fields of science, e.g., for simulations of electrical circuits or micromechanical devices. It is interesting to note that although these simulations are very close to the RRGM approach, there appear to be little or no knowledge of the advances in the other field.

In the next section reduced-order modeling of linear dynamical systems will be reviewed, and the close analogy to the RRGM-type methods will be pointed out in section 3. Section 4 deals with the problem when to stop the recursions. How do we know that our Green's function matrix element has converged? Using results from reduced-order modeling, we propose a stopping criterion for the RRGM recursions, on the basis of an upper bound to the absolute error. In section 5 the error bound is tested on several molecular problems, both bound and scattering states. The role of the start-vector for the convergence is discussed in section 6, and section 7 contains a summary and discussion of the results.

II. Reduced-Order Modeling

To simulate large-scale dynamical systems arising from, e.g., circuit simulations, structural dynamics and micromechanical systems, reduced-order models (ROM) have been of great use. The publications in the field range from large scale simulations to mathematical analysis and development of novel computational methods. The recent monograph by Antoulas[39] gives a good overview of the field. Below the ROM is reviewed with emphasis on the close relation to quantum dynamics in general and the RRGM in particular. The presentation follows closely

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the review by Bai.[40] The notation in this section follows that used in ROM and differs from that used in other sections of the paper.

The underlying idea in ROM is to replace a large and complex dynamical system with a system of the same type, with a much smaller state-space dimension but that preserves essential properties. A continuous time-invariant multi-input, multi-output linear dynamical system can be written as

$$\mathbf{C}\frac{\mathrm{d}x(t)}{\mathrm{d}t} + \mathbf{G}x(t) = \mathbf{B}u(t) \tag{1}$$

$$y(t) = \mathbf{L}^{\mathrm{T}}x(t) \tag{2}$$

Here **C** and **G** are $N \times N$ system matrices and **B** and **L** are input and output distribution arrays, respectively. The system matrices **C** and **G** are allowed to be singular as long as $\mathbf{G} + s\mathbf{C}$ is regular, i.e., singular for a finite number of complex shifts s. Taking the Laplace transform of (1) leads to the frequency domain formulation

$$s\mathbf{C}X(s) + \mathbf{G}X(s) = \mathbf{B}U(s) \tag{3}$$

$$Y(s) = \mathbf{L}^{\mathrm{T}}X(s) \tag{4}$$

where $X(s)$ is the Laplace transform of $x(t)$. By eliminating $X(s)$ from eq 3, we see that the system input **B** and output **L** vectors are related via

$$Y(s) = Z(s)\,U(s) \tag{5}$$

$$Z(s) = \mathbf{L}^{\mathrm{T}}(\mathbf{G} + s\mathbf{C})^{-1}\mathbf{B} \tag{6}$$

where $Z(s)$ is the transfer function. There are two essential properties of the linear dynamical system (1) that must be preserved in using ROM: stability and passivity. A linear system is stable if all eigenvalues have nonpositive real parts and all pure imaginary eigenvalues have multiplicity one. A system is passive if the energy is conserved, i.e., the transfer function $Z_t(s)$, eq 6, is positive and real.

Consider, for ease of discussion, the symmetric single-input, single output $\mathbf{B} = \mathbf{L} = \mathbf{b}$ case. Assume further that **C** and **G** are symmetric and positive semidefinite. Let

$$\mathbf{A} = (\mathbf{G} + s_0\mathbf{C}) = \mathbf{M}\mathbf{M}^{\mathrm{T}} \tag{7}$$

where s_0 is an arbitrary complex shift and $\mathbf{M}\mathbf{M}^{\mathrm{T}}$ is a Cholesky decomposition. Note that **A** is also symmetric and positive semidefinite. The transfer function can then be written

$$Z(s) = \mathbf{b}^{\mathrm{T}}(\mathbf{G} + s_0\mathbf{C} + (s - s_0)\mathbf{C})^{-1}\mathbf{b} \tag{8}$$

$$= \mathbf{b}^{\mathrm{T}}(\mathbf{M}\mathbf{M}^{\mathrm{T}} + (s - s_0)\mathbf{C})^{-1}\mathbf{b} \tag{9}$$

$$= \mathbf{l}^{\mathrm{T}}(I + (s - s_0)\mathbf{A})^{-1}l \tag{10}$$

with $\mathbf{A} = \mathbf{M}^{-1}\mathbf{C}\mathbf{M}^{-\mathrm{T}}$ and $\mathbf{l} = \mathbf{M}^{-1}\mathbf{b}$. The transfer function $Z(s)$ is a rational function of order N and can be computed via a low-order matrix-Padé approximation of $Z(s)$, capturing the essential input-output characteristics. An efficient method to compute (8) is the symmetric Padé-via-Lanczos (PVL) method by Freund and co-workers.[41,42] The idea behind the PVL is to build a low dimensional Krylov space with $\mathbf{l} = \mathbf{M}^{-1}\mathbf{b}$ as start-vector $\mathbf{v}_0$ to the Lanczos algorithm[2]

$$\beta_{n+1}\mathbf{v}_{n+1} = (\mathbf{A} - \alpha_n)\mathbf{v}_n - \beta_n\mathbf{v}_{n-1} \tag{11}$$

$$\alpha_n = \mathbf{v}_n^{\mathrm{T}}\mathbf{A}\mathbf{v}_n \qquad \beta_n = ||\mathbf{v}_n||_2 \tag{12}$$

$$\mathbf{V}_n = [v_0\ v_1 \ldots v_{n-1}] \qquad \mathbf{T}_n = \mathbf{V}_n^{\mathrm{T}}\mathbf{A}\mathbf{V}_n \tag{13}$$

V is the matrix of orthonormal Lanczos vectors. After n Lanczos recursions, the nth matrix-Padé approximant of the transfer function (8) can be written

$$Z(s) = \rho^{\mathrm{T}}(I_n + (s - s_0)\mathbf{T}_n)^{-1}\rho \tag{14}$$

$$= {\beta_1}^2(I_n + (s - s_0)\mathbf{T}_n)_{1,1}{}^{-1} \tag{15}$$

$$= \rho^{\mathrm{T}}\mathbf{S}(I_n + (s - s_0)\mathbf{E}_n)^{-1}\mathbf{S}^{\mathrm{T}}\rho \tag{16}$$

where $\rho = \mathbf{V}_n^{\mathrm{T}}\mathbf{l}$. Notice that, as indicated in eq 15, if the Lanczos algorithm is initiated by $\mathbf{v}_0 = \mathbf{l}$ we have that $\rho = [\beta_1\ 0\ 0\ ...]$ and the transfer function is the (1, 1) entry of the resolvent matrix. The Lanczos matrix can, in turn, be decomposed using the Ritz eigenstates $\mathbf{T}_n = \mathbf{S}_n\mathbf{E}_n\mathbf{S}_n^{\mathrm{T}}$. The Lanczos algorithm converges first close to the (arbitrary) complex shift s_0. The PVL preserves stability and passivity of the underlying dynamical system. To ensure that $\mathbf{T}_n$ remains positive semidefinite despite round-off errors the coupled two term version of the Lanczos algorithm can be used.[43] Instead of generating entries of a tridiagonal matrix $\mathbf{T}_n$ it directly computes a decomposition $\mathbf{T}_n = \mathbf{L}_n^{\mathrm{T}}\mathbf{D}\mathbf{L}_n$ which by construction is positive semi-definite. Here **L** is upper triangular and **D** is a diagonal matrix.

The PVL transfer function (14) can be solved either via an eigenvalue decomposition of $\mathbf{T}_n$, by solving a set of linear systems $(s - s_0)\mathbf{T}_n x = \mathbf{l}$ for all values of s or using continued-fraction techniques.[27] The PVL formalism is easily extended to multiple input-output systems using a band-Lanczos algorithm.[37,41]

III. RRGM and ROM

The ROM and RRGM methods are very similar. The linear dynamical system used in chemical dynamics is the Schrödinger equation, which in the time-independent formulation reads

$$E\Psi(E) - H\Psi(E) = \Phi_i \tag{17}$$

Comparing this equation with eq 3 it is clear that the transfer function (6), with Φ_{i} as initial (input) and Φ_{f} as final (output) states, is nothing but the correlation function

$$C(E) = \Phi_{\mathrm{f}}^{\mathrm{T}}(EI - H)^{-1}\Phi_{\mathrm{i}} \tag{18}$$

and that the symmetric PVL expression (14) is the RRGM autocorrelation function[1]

$$C(E) = \rho^{\mathrm{T}}(EI_n - T_n)^{-1}\rho \tag{19}$$

$$= {\beta_1}^2\sum_{k=0}^{n} {S_{1k}}^2(E - E_n)^{-1} \tag{20}$$

where $S_{1k}{}^2$ are the residues and E_n the poles.

The RRGM and ROM methods have been developed in parallel in different scientific fields. It is thus natural that the development has focused on different issues. In ROM there are mathematical proofs and analyses regarding stability, applicability and convergence of the computational methods. The matrices come from many different scientific areas and have different properties, and a vast set of tools from numerical linear algebra,

e.g., Cholesky and LU decompositions, are used. The matrices are often small enough to be stored, at least in sparse matrix format. The RRGM, on the other hand, considers only Hamiltonian matrices and is more concerned with applying the method than to analyze its properties. The discretization of the underlying multidimensional molecular Hamiltonian leads to very large matrices where the Hamiltonian cannot be explicitly stored and only is accessible in a matrix-vector subroutine.

IV. Error Bounds and Stopping Criteria

In the RRGM literature there are today, to our knowledge, no objective criteria to check for convergence of the correlation function and to determine when to stop the recursions, with the exception of the work of Meyer and Pal.[44] Considering only the convergence of the eigenvalues can be misleading, as they give no information about how the residues converge. Comparing the correlation function for two different recursion steps is not recommended because the recursive method could just have stagnated due to loss of orthogonality and the fact that extreme states converge first.

In the ROM-literature convergence of the computational schemes are an important issue. For the transfer function computed via PVL, eq 14, Bai and co-workers[45,46] derived an estimate for the absolute error $|Z_n(s) - Z(s)|$, and used it as a stopping criteria. With the close analogy between the ROM and RRGM methods, it should be possible, after some small modifications, to apply their result to RRGM-type problems in quantum dynamics.

On the basis of the result by Bai and co-workers,[45,46] we propose that the error for the correlation function (18), after n Lanczos recursions, can be approximated as

$$|C_n(E) - C(E)| \le \beta_0 |E^2| \frac{|\tau_{1n}\tau_{n1}|}{|E - ||H||\,|} \tag{21}$$

$$\tau_{1n} = \mathbf{e}_1^{\mathrm{T}}(E - T_n)^{-1}\mathbf{e}_n \tag{22}$$

where $\mathbf{e}_1^{\mathrm{T}} = (1, 0, ..., 0)$ and $\mathbf{e}_n^{\mathrm{T}} = (0, 0, ..., 1)$. For symmetric input−output functions $\tau_{1n} = \tau_{n1}$. The matrix norm $||H||$ is computed via Hager and Highhams's norm estimator.[47] The denominator $|E - ||H||\,|$ contributes mainly close to convergence, whereas it is τ_{1n} that determines the general behavior. To compute τ_{1n} from an eigenvalue decomposition

$$\tau_{1n} = \mathbf{e}_1^{\mathrm{T}}(E - T_n)^{-1}\mathbf{e}_n = \sum_{k=1}^{n} S_{1k}S_{nk}/(E - E_k) \tag{23}$$

the first and last row of the eigenvector matrix **S** are needed. As noted by Smith et al.[48] the QL-algorithm can be modified to compute both S_{1k} and S_{nk} alongside the eigenvalues at, essentially, no extra cost. As a bonus, an estimate for the error of the eigenvalue E_k, given by $|S_{nk}|^2\beta_n$, is obtained.

V. Numerical Experiments

A problem with the RRGM is that there is no way to indicate when to stop the recursions, i.e., when the correlation function has converged. If the proposed error bound could be used as a stopping criteria, it would be an invaluable tool, making it possible to stop the recursions at a predefined error tolerance. To test the error bound, eq 21, four different molecular systems were studied, two with bound states and two scattering problems. For the bound states the Rb_2 diatom and the H_2O molecule was used and for the scattering problems $H + H_2$ and CO_2 were studied. Issues to be considered are how close the error bound is to the true error and effects of loss of orthogonality.

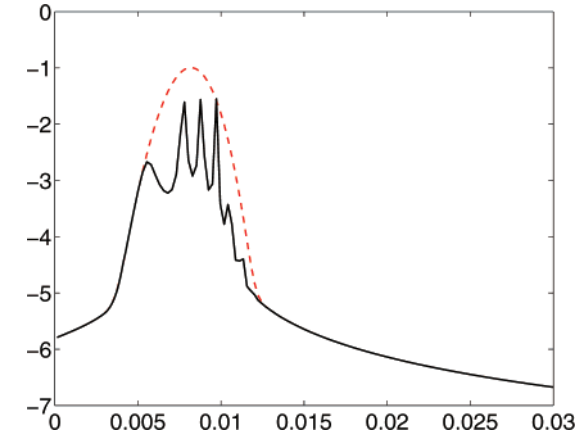

Figure 1. Logarithm of the line shape function for the Rb_2 diatom with $N = 2048$. Solid line: RRGM after 400 recursions. Dashed line: Exact result.

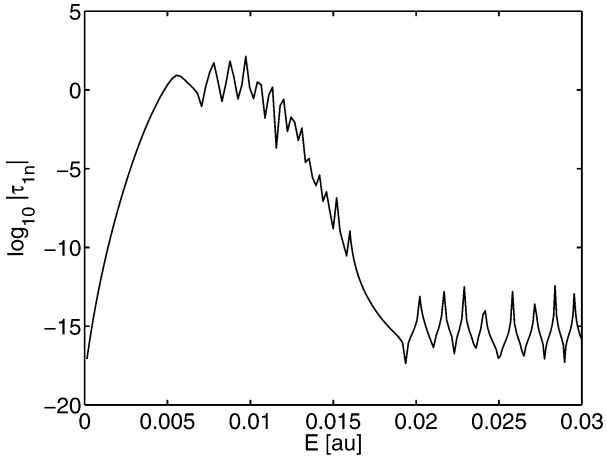

Figure 2. Function τ_{1n} (22) after 400 recursions.

A. Rb_2. As a first test case the rubidium diatom was chosen because it is small enough to allow for direct computation of eigenstates and correlation functions, yet has properties similar to those of large molecular systems. A grid with $N = 2048$ grid points was used with a pseudospectral discretization for the kinetic energy. The potential curve for the electronic ground state for Rb_2 was taken from Park et al.[49] and a Gaussian was chosen as the initial state. The line shape function,[24] expressed in terms of energies E and residues (Frank-Condon factors) r_k^2, is given as

$$I(E) = \sum_k r_k^2 \frac{\Gamma^2}{(E - E_k)^2 + \Gamma^2} \tag{24}$$

The line shape function is plotted in Figure 1. The dashed line is the exact result and the solid line is the result after 400 Lanczos recursions. The function τ_{1n}, also after 400 recursions, is shown in Figure 2. In Figure 3 the error estimate for $E_0 = 0.083$ eV, corresponding to the maximum of the line shape function, is shown. The error estimate (21) oscillates initially before decaying fast, whereas the true error is constant until convergence sets in. The reason for this behavior is that initially there are no Ritz eigenvalue close to E_0, and the line shape function is close to zero, thus the large, nearly constant, true error and the oscillations in the upper bound. Once the Ritz eigenstate starts to converge, both the exact and the estimated

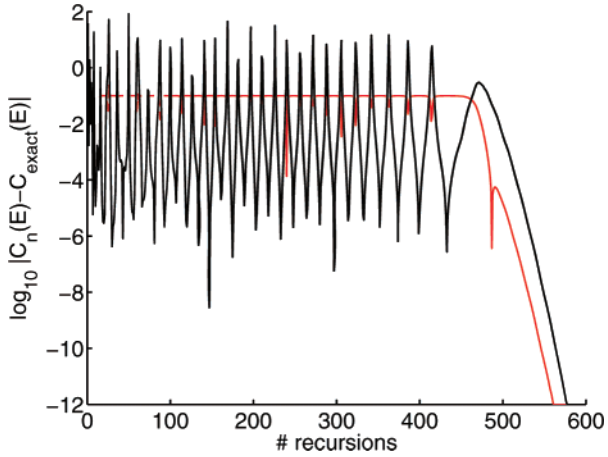

Figure 3. Error of the line shape function $I(E)$ for $E = 0.083$ as a function of the number of recursions. Solid line: estimated error from eq 21. Dashed line: true error.

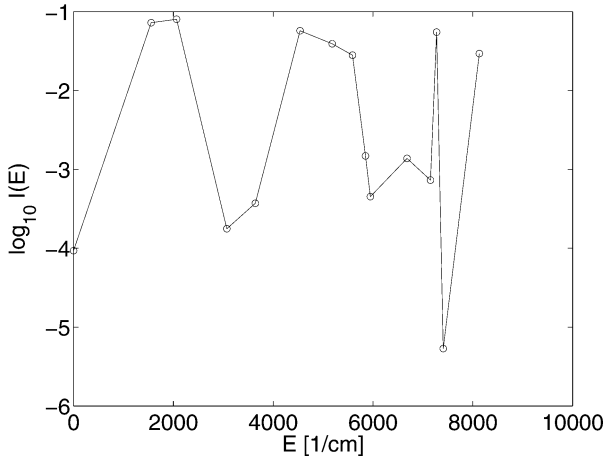

Figure 4. Line shape function $I(E)$ for H_2O for $E < 10\,000$ cm^{-1} with a Gaussian initial state. $I(E)$ is computed at the Ritz eigenvalues and joined by lines to guide the eye.

error decays fast. This is well-known for eigenvalues where the error estimate $|S_{nk}|^2\beta_n$ gives a too low value initially but provides an upper bound when it starts to converge.[50] Compared to the true error, the error estimate leads to about 30 extra recursions. Thus the error estimate can be used as a stopping criteria.

B. H_2O. As a more challenging problem the vibrational states of the water molecule was considered. Radau coordinates and the Partridge−Schwenke potential energy surface were used, following Chen and Guo.[51] For the radial coordinates 64 grid points were used and 32 Legendre polynomials for the bending angle, leading to a grid size of 131 072. Only states of even symmetry were considered. This basis size allows for converged states up to 20 000 cm^{-1}. A Gaussian initial state was used and the line shape function (24) was computed at the Ritz eigenvalues up to 10 000 cm^{-1}. The converged result is depicted in Figure 4. For this system we are interested in how fast the transfer function converges for the different poles and also how the convergence is affected by loss of orthogonality between the Lanczos vectors.

In Figure 5 the error estimates are shown for 100, 200, and 300 Lanczos recursions using full re-orthogonalization. In Figure 6 the same is depicted but with no re-orthogonalization. The line shape converges faster for lower energies, as expected. It is also clear that the loss of orthogonality, leading to multiple copies of eigenstates, slows down convergence significantly.

C. $H + H_2$. For scattering problems in quantum dynamics, discretized on a grid and with absorbing potentials or complex

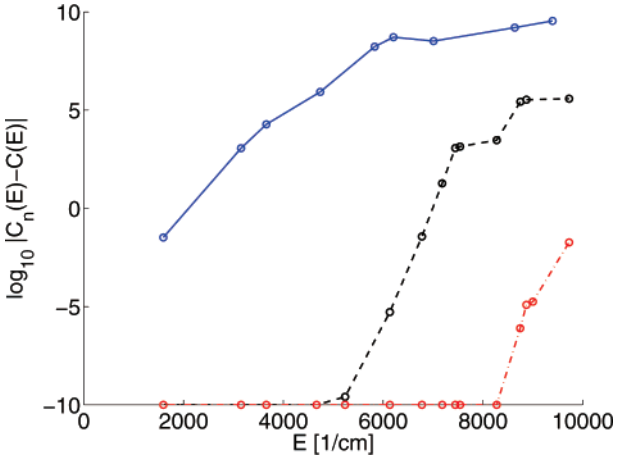

Figure 5. RRGM with full re-orthogonalization. The estimated error, using eq 21, for 100, 200, and 300 recursions.

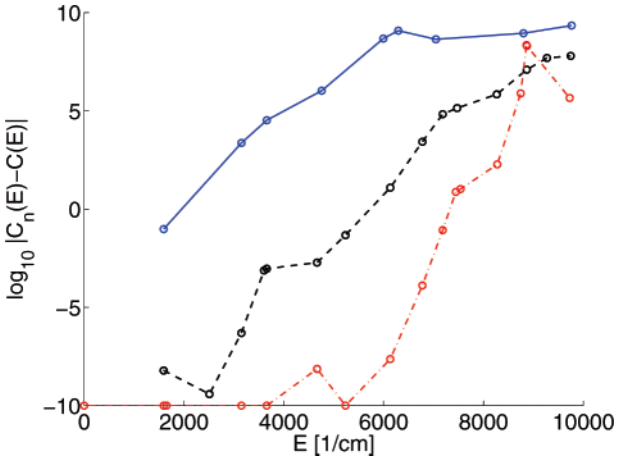

Figure 6. RRGM with no re-orthogonalization. The estimated error, using eq 21, for 100, 200, and 300 recursions.

scaling, the bi-orthogonal scalar product, i.e., without complex conjugation, is used. This is typically not done in ROM and the expression for the upper bound must be validated. As a first test case the collinear $H + H_2$ system was considered. The Hamiltonian was discretized on a 80×80 grid using the LSTH surface and pseudo-spectral discretization.[38] A quartic absorbing potential was used to ensure outgoing boundary condition and a Gaussian was used as initial state. A reference solution was obtained by solving a set of linear equations with high accuracy. In Figure 7 the absolute value of the complex Green's function (18) is plotted. In Figure 8 the true error and the error estimate are plotted after 300 recursions. Except for high energies, where the RRGM is far from convergence, the true error is below the estimated error; i.e., once the method starts to converge, the error estimate gives an upper bound and can be used as a stopping criteria. Both full and no re-orthogonalization were considered and the error estimate is depicted in Figures 9 and 10, respectively. It is clear that the loss of orthogonality slows down convergence significantly also in this case. The stopping criteria results in about 10−20 more recursions than the true error would have given, depending on the energy.

D. CO_2. As a final test the collinear CO_2 was considered. Jacobi coordinates on a 256×256 grid with absorbing potential was used.[52] The lowest vibrational state on the ground electronic state was used as the initial state, assuming a δ-pulse excitation. Here the imaginary part of the Green's function Im $G(E)$ was considered, depicted in Figure 11. The error after 5000, 10 000, and 15 000 recursions is shown in Figure 12. After 15 000

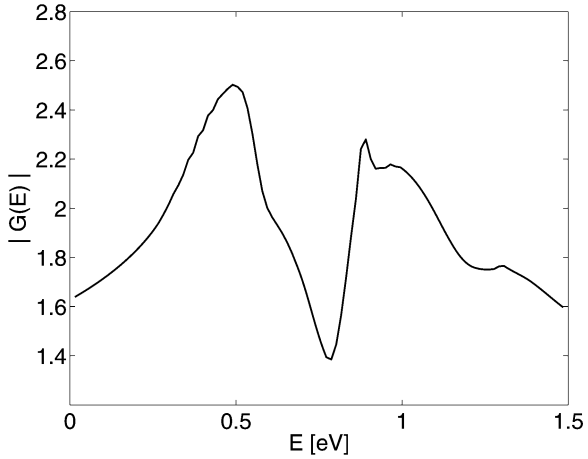

Figure 7. Absolute value of the Greens function for the collinear H + H_2 using a Gaussian initials state.

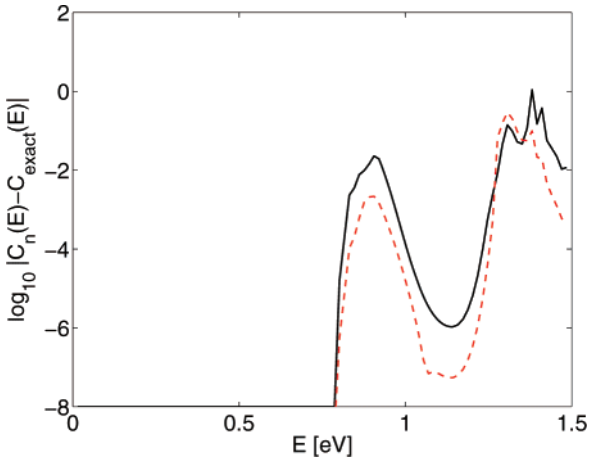

Figure 8. Comparison between the estimated (solid line) and true (dashed line) error after 800 recursions.

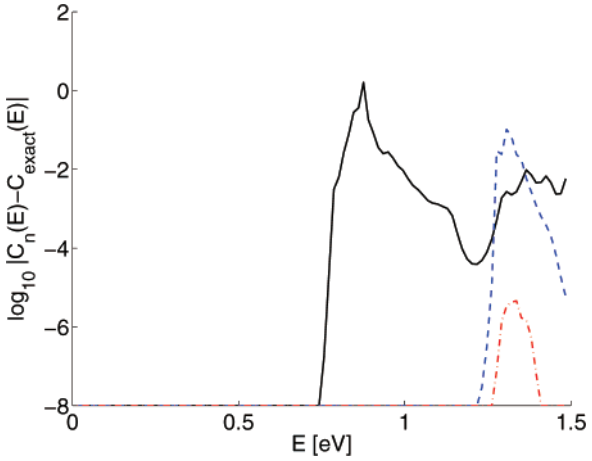

Figure 9. RRGM with full re-orthogonalization. The estimated error, using eq 21, for 500, 800, and 1100 recursions.

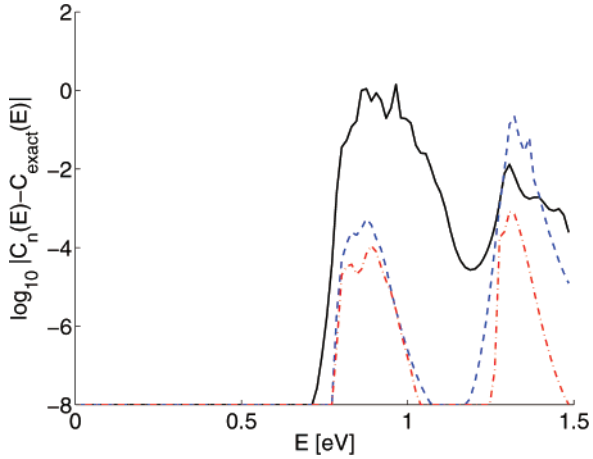

Figure 10. RRGM with no re-orthogonalization. The estimated error, using eq 21, for 500, 800, and 1100 recursions.

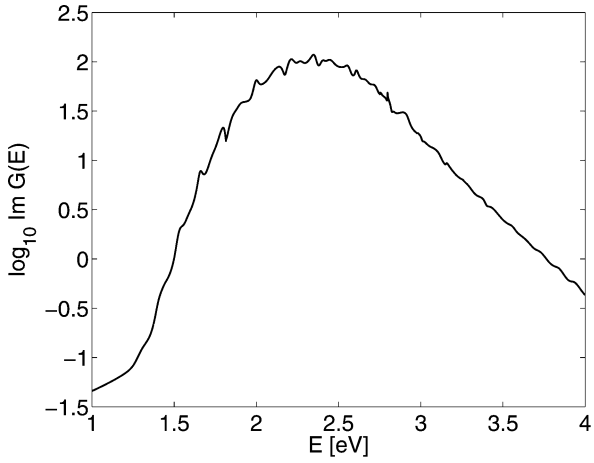

Figure 11. Imaginary part of the Green's function Im $G(E)$ for the CO_2 molecule.

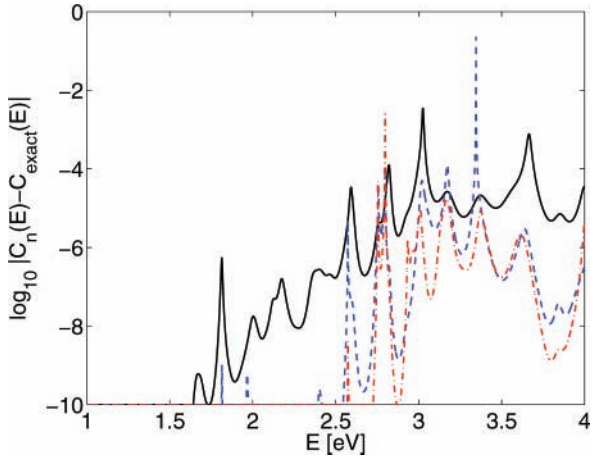

Figure 12. Estimated error for 5000 (solid line), 1000 (dashed line), and 15 000 (dash-dotted line) RRGM recursions, for the CO_2 molecule.

recursions the photodissociation cross-section was only converged up to 2.5 eV.

VI. The Role of the Start-Vector

In the earlier literature on RRGM[1,22−24] there were a belief that the states with largest overlap with the start-vector would converge first. Stated differently, if a start-vector was constructed as $\Psi = \sum_n c_n \phi_n$, the states with largest $|c_n|$ would converge first and the Lanczos recursions would stop when all states with $|c_n|$ > 0 had been found. Unfortunately, this is not true. In Figure 13 the projection of the true eigenstates of the Rb_2 system onto the first and the 10th Lanczos vector are shown. Full orthogonalization is used. After only 10 recursions do the extreme eigenstates dominate the current Lanczos vector and converge first, even though they had $c_n = 0$ and were not present in Ψ. The consequence of this is that if the Hamiltonian has a large spectral width, the convergence of extreme, unphysical states will slow down the convergence of, e.g., the line shape function. To overcome this and improve the convergence rate, different

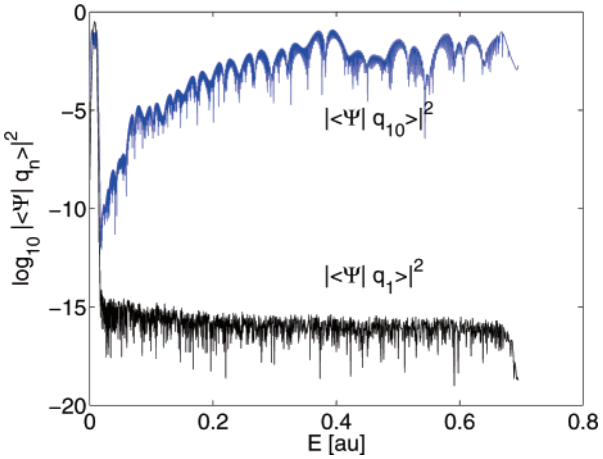

Figure 13. Projection $|\Psi_k|q_n\rangle|$ of the Lanczos vector $|q_n\rangle$ onto the true eigenvectors $|\phi_k\rangle$ of the system, for the start-vector $k = 1$, and the 10th Lanczos vector $k = 10$. The same setup as in Figure 1 is used.

filtering functions $f(H)$ could be used instead of H in the Lanczos algorithm,[53−56] steering the convergence to the spectral region of interest. The drawback is that each application of the filter requieres several applications of the Hamiltonian matrix.

VII. Summary

The recursive residue generation method opened up for the ability to compute spectral properties of very large Hamiltonian systems, for both bound and scattering states. In a parallel scientific field, reduced-order modeling was developed, resulting in novel computational schemes and mathematical analysis. It is clear that interaction between the two fields could lead to great benefits. One such cross-fertilization is discussed in this paper, namely the ability to have an objective stopping criteria for the RRGM recursions. It was shown that the error bound, derived for large-scale linear dynamical systems, is easily carried over to the Schrödinger equation and quantum dynamics and works well for both bound and scattering states. We further showed that states contained in the start-vector do not converge first. It is the extreme states that converge first, regardless of the initial state.

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References and Notes

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