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Correlation Functions and Thermal Rate Constants[†]

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Thermal rate constants $k(T)$ and cumulative reaction probabilities $N(E)$ can be computed as a sum of correlation functions $C_{nm} = \langle\phi_n|f(\hat{H})|\phi_m\rangle$. In this paper we discuss the use of two different Krylov subspace methods to compute these correlation functions for large systems. The first approach is based on the Lanczos algorithm to transform the Hamiltonian to tridiagonal form. As shown by Mandelshtam (*J. Chem. Phys.* **1998**, *108*, 9999) and Chen and Guo (*J. Chem. Phys.* **1999**, *111*, 9944), all correlation functions can be computed from a single recursion. The second approach treats a number of linear systems of equations using a Krylov subspace solver. Here the quasiminimal residual (QMR) method was used. For the first approach, we found that we needed the same number of Lanczos recursions as the size of the matrix. If no re-orthogonalization is used, the number of recursions grows further. The linear solver approach, on the other hand, converges fast for each linear system, but many systems must be solved.

I. Introduction

Correlation functions play an important role in chemical physics. They can be used to describe state-to-state, initial state selected and cumulative reaction probabilities, photodissociation, resonance Raman cross-sections and Golden Rule type expressions, to mention a few.[1] Assuming a time-independent Hamiltonian $\hat{H}$, we define the correlation function between states $|\phi_n\rangle$ and $|\phi_m\rangle$ as

$$C_{nm} = \langle\phi_n|f(\hat{H})|\phi_m\rangle \tag{1}$$

Here we will concentrate on the time-evolution operator $\hat{U}(t,t_0)$ and the Greens function $\hat{G}(E)$ although $f(\hat{H})$ can be any (analytic) function of the Hamiltonian. The two operators are defined as

$$\hat{U}(t,t_0) = \exp[-i\hat{H}(t - t_0)/\hbar] \tag{2}$$

and

$$\hat{G}(E) = \lim_{\epsilon\rightarrow 0}[E\hat{1} - \hat{H} + i\epsilon]^{-1} \tag{3}$$

and are related through the (half) Fourier transform[1]

$$\hat{G}(E) = (i\hbar)^{-1}\int_0^\infty dt\, e^{iEt/\hbar}\hat{U}(t,0) \tag{4}$$

The standard textbook approach to compute correlation functions is to diagonalize the Hamiltonian matrix (represented in a suitable basis or grid discretization) and to express, e.g., the time evolution operator in this eigenbasis

$$e^{-iH(t-t_0)/\hbar} = V\, e^{-i\Lambda(t-t_0)/\hbar}V^\dagger \tag{5}$$

Here Λ is the eigenvalue and V the eigenvector matrix. Although appealing from a theoretical point of view, the method is of no practical use for realistic systems. It is simply not feasible to compute all eigenvalues and eigenvectors of matrices with dimension $N > 10^3 \sim 10^4$. To overcome this limitation, Wyatt and co-workers derived the recursive residue generation method (RRGM).[2] In the RRGM, the Lanczos algorithm (see below) is used to reduce recursively the effective dimension of the problem so that, via diagonalization of a small tridiagonal matrix, the correlation functions can be computed. The RRGM was originally designed for diagonal correlation functions, even though nondiagonal elements can be computed using so-called residue algebra.[2] In many applications, we need also to compute nondiagonal correlation functions. Recently, Mandelshtam[3] pointed out, using Chebychev polynomials, that the scalar products between the recursively generated vectors $|n\rangle$ and the states $|\phi_m\rangle$ can be computed on the fly without the explicit need to store all of the recursion vectors. This has the important consequence that *all* correlation functions C_{nm} can be computed from a *single* recursion. Chen and Guo[4] showed that this can also be implemented for the Lanczos algorithm.

In this paper we will discuss how Krylov subspace methods can be used to compute thermal rate constants through correlation functions. In Section 2 we review the Lanczos algorithm for computing eigenvalues and solving linear systems. In Section 3 the cumulative reaction probability is formulated in terms of a sum over correlation functions using the Greens function (eq 3). Numerical experiments are reported in Section 4, and concluding remarks are given in Section 5.

II. The Lanczos Algorithm

In the Lanczos algorithm,[5] a new orthogonal basis V is generated recursively from a given initial vector $|0\rangle$, leading to a tridiagonal representation T of the Hamiltonian. By diagonalizing the Lanczos matrix $T = S\Lambda S^\dagger$ we can write

$$C_{nm} = \langle\phi_n|f(H)|\phi_m\rangle = \langle\phi_n|Vf(T)V^\dagger|\phi_m\rangle = \langle\phi_n|VSf(\Lambda)S^\dagger V^\dagger|\phi_m\rangle \tag{6}$$

In the ideal case, the number of recursions M for C_{nm} to converge is much lower than the size N of the Hamiltonian matrix. The procedure can be initialized by any vector $|0\rangle$, and the orthonormal Lanczos vectors V will differ depending on the

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choice of initial state. In scientific computing it is often chosen as a random vector so that it has nonzero projection on all eigenstates of the system. The Lanczos algorithm is given by the three-term recurrence relation

$$\beta_{n+1}|n+1\rangle = (H - \alpha_n)|n\rangle - \beta_n|n-1\rangle \tag{7}$$

$$T_{n,n} = \alpha_n = \langle n|H|n\rangle \tag{8}$$

$$T_{n,n+1} = T_{n+1,n} = \beta_n = ||\ |n+1\rangle\ || \tag{9}$$

and $V = \{|0\rangle,|1\rangle,|2\rangle,...|M\rangle\}$ after M recursions. The α_n can be viewed as eigenenergies in a linear chain with β_n as coupling strengths. In the RRGM[2], $|\phi_m\rangle$ is used to initialize the recursion which simplifies the expression (eq 6) for the (diagonal) correlation function to

$$\begin{aligned} V^{\dagger}|\phi_m\rangle &= \{\langle 0|,\langle 1|,\langle 2,...\}|\phi_m\rangle = (1,0,0,...)^T \\ C_{mm} &= \langle\phi_m|VSf(\Lambda)S^{\dagger}V^{\dagger}|\phi_m\rangle = (Sf(\Lambda)S^{\dagger})_{1,1} \\ &= \sum_n |S_{1n}|^2 f(\Lambda_n) \end{aligned} \tag{10}$$

Thus, only the (1,1) element of the correlation function is needed and only the first row of the eigenvector matrix needs to be computed.[2] For the Greens function (eq 3), one does not even have to diagonalize the Lanczos matrix because the matrix element can be computed from a continued fraction expansion.[6,7] In exact mathematics, the Lanczos recursion stops after (maximum) N iterations, i.e., the size of the original matrix. The outer eigenstates of H converge first, whereas inner (and closely spaced) states converge more slowly. If information of the system can be incorporated in the initial state, the number of recursions might be considerably fewer than the matrix size. Examples include slightly perturbed Hamiltonians $H = H_0 + V$ where eigenstates to H_0 can be used to initialize the recursion.[7] This is in contrast to the Chebychev polynomials[3] whose recursion scheme depends only on the spectral range of the underlying Hamiltonian. The drawback of the Lanczos method is that in numerical implementations there will be a loss of orthogonality between the generated vectors. This leads to spurious and multiple copies of eigenstates, and the number of recursions might be larger than the matrix size ($M > N$). But the spurious states have zero overlap with the initial state and can easily be removed, and the residues for the multiple copies add up to the correct value.[2] The standard way to monitor convergence is to diagonalize the Lanczos matrix and compute C_{nm} for several different steps in the recursion.[4] This could be costly for large systems, and a computable expression for an upper bound to the correlation function would be of great use.

In the approach described above, we try to find a factorization of the Hamiltonian that after $M \ll N$ steps contains the essential information of the system, with respect to the start vector. Another approach is to use the Lanczos algorithm to solve linear systems of equations $Ax = b$. (For the problems considered here, this corresponds to $(E - H)|\phi_m(E)\rangle = |\phi_m\rangle$). In this approach, a distance, the residual $r_M = b - Ax_M$, is minimized in each step with the solution x approximated by the vector x_M after M recursions. The algorithm can be described in a compact form as follows (e_1 is the unit vector $(1,0,0...)^T$)

1. Perform M step of the Lanczos algorithm with b as start vector. This gives $T_M = V_M^{\dagger}HV_M$.

2. Find the vector y that minimizes the residual norm $||r_M|| = ||T_My - ||b||e_1||$.

3. If converged, compute the solution from $x_n = Vy$, else set $M = M + 1$ and go to 1.

The minimization is done in a least-squares sense using a QR factorization. If full orthogonalization is used, this scheme corresponds to the generalized minimal residual (GMRES) method.[18] (GMRES is actually built on the Arnoldi method which reduces to the Lanczos method for Hermitean matrices.) The GMRES is guaranteed to converge in a maximum of N iterations, and the residual norm decreases monotonically. The drawback is that all of the generated Krylov vectors must be stored and orthogonalized to all previous vectors. Thus, both memory requirements and CPU time per iteration grow linearly with time. This can be overcome by restarting the method every Mth step, but this can slow convergence considerably. If we choose not to store the Lanczos vectors (with subsequent loss of orthogonality), we cannot truly minimize the residual norm $||r_M||$, but we can minimize a similar norm that is not so far from the true residual norm. This is the idea behind the quasiminimal residual (QMR) method.[16] The QMR has a constant need of memory and CPU time per iteration, which make it very suitable for large systems. It needs more iterations than the GMRES to converge, but our experience[17] is that the total CPU time can be significantly less (because no Gram-Schmidt orthogonalization is needed).

We can thus compute correlation functions using two different Lanczos-based approaches: a factorization to tridiagonal form and by solving a set of linear system of equations. The factorization has the advantage of giving the correlation function $C_{nm}(E)$ for all energies at once, but there are no error bounds and a large number of iterations might be needed. The linear solver on the other hand can only be solved for a single vector at a time, but the minimization property leads to a significantly smaller number of recursions and there are error bounds on the residual.

III. Cumulative Reaction Probabilities

Miller, Schwartz, and Tromp[8] showed that the thermal rate constant $k(T)$ can be computed from a Boltzmann average of the cumulative reaction probability $N(E)$

$$k(T) = Q^{-1}\int \mathrm{d}E\ \mathrm{e}^{-\beta E}N(E) \tag{11}$$

where Q is the reactant partition function and $N(E)$ can be computed as the trace

$$N(E) = \frac{1}{2}(2\pi\hbar)^2\mathrm{Tr}[\hat{F}\delta(E - \hat{H})\hat{F}\delta(E - \hat{H})] \tag{12}$$

where $\hat{F}$ is a flux operator. A number of different procedures have been developed for computing $N(E)$. Manthe and Miller[9] applied the Lanczos method to the expression inside the trace in eq 12 to compute $N(E)$. In each recursion step, the action of two δ-functions (in a suitable representation) must be computed. This can be done efficiently using Lanczos subspace methods as QMR[16,17] and GMRES.[18] Another approach to compute the trace is to use the properties of the flux operator $\hat{F}$.[1,10-13] It can be shown[11,14] that in a real finite basis, the flux operator

$$\hat{F} = \frac{1}{2m}[\hat{p}_F\delta(q_F) + \delta(q_F)\hat{p}_F] \tag{13}$$

has only two nonzero eigenvalues (q_F is the reaction coordinate and $\hat{p}_F$ the momentum operator along that coordinate). The eigenvalues are equal in magnitude but with opposite sign. In a multidimensional, case the flux operator will not be of low rank because the two flux eigenstates will be repeated for every state in the perpendicular degree of freedom. The flux operator (eq 13) can equivalently be written as[8]

$$\hat{F} = \frac{i}{\hbar}[\hat{T}, h(q_0)] \tag{14}$$

where $\hat{T}$ is the kinetic energy and $h(q_0)$ is the Heaviside step function. The two forms, eqs 13 and 14, do not have identical numerical properties in a basis set representation. The second form has a rank higher than two, even though the states decrease quickly in magnitude. Miller and Carrington[13] computed the eigenstates to the flux operator (eq 13) in a finite basis representation, and then transformed the eigenstates to the DVR, retaining a rank of 2 for the flux operator. We have used the form of eq 14 because it generalizes better to higher dimensions and has better numerical properties.[15]

Using the flux eigenstates $\hat{F}|\phi_n\rangle = \lambda_n|\phi_n\rangle$ we can write $N(E)$ in two was:[1,10−13] either as a sum of expectation values of the flux operator

$$\begin{aligned} N(E) &= \frac{1}{2}(2\pi\hbar)^2 \sum_n \lambda_n \langle\phi_n|\delta(E - \hat{H})\hat{F}\delta(E - \hat{H})|\phi_n\rangle \qquad (15) \\ &= \frac{1}{2}(2\pi\hbar)^2 \sum_n \lambda_n \langle\phi_n(E)|\hat{F}|\phi_n(E)\rangle \end{aligned}$$

or as a sum of (energy) correlation functions

$$\begin{aligned} N(E) &= \frac{1}{2}(2\pi\hbar)^2 \sum_n \sum_m \lambda_n \lambda_m |\langle\phi_n|\delta(E - \hat{H})|\phi_m\rangle|^2 \qquad (16) \\ &= \frac{1}{2}(2\pi\hbar)^2 \sum_n \sum_m \lambda_n \lambda_m |\langle\phi_n|\phi_m(E)\rangle|^2 \end{aligned}$$

The δ-function can be represented in a time-independent framework from the Greens function as $\delta(E - \hat{H}) = -{}^1/_\pi Im\hat{G}(E) = -{}^1/_\pi \hat{G}_i(E)$. Using this representation, the Lanczos method can be used to compute $N(E)$ either from an expansion in a Lanczos basis (eq 6) or from solving the linear system of equations $|\phi_m(E)\rangle = \hat{G}_i(E)|\phi_n\rangle$. Combining eqs 16 and 6 we can compute $N(E)$ from

$$N(E) = 2\hbar^2 \sum_n \sum_m \lambda_n \lambda_m |\langle\phi_n|VS[E - \Lambda]^{-1} S^\dagger V^\dagger|\phi_m\rangle|^2 \tag{17}$$

After the Lanczos matrix has been diagonalized, $N(E)$ is given for *all* energies at once. Computationally, there are several issues to consider. First, how many iterations do we need to get a converged result? Can we find a start vector $|0\rangle$ that improves the convergence rate with respect to the number of iterations? How many more iterations $M > N$ do we need? A problem is to find a nonexpensive way to check for convergence.

Another approach is to compute $|\phi_m(E)\rangle$ from which (eq 16) can be computed. Using the linear solver approach it is important to remember that, in general, $Im[G(E)]|\psi\rangle \neq Im[G(E)|\psi\rangle]$. Instead, the form $Im[G(E)] = {}^i/_2[G(E)^* - G(E)]$ should be used. From this, the matrix elements $\langle\phi_n|\phi_m(E)\rangle$ can be computed as

$$\begin{aligned} \langle\phi_m|Im[G(E)]|\phi_n\rangle &= \frac{i}{2}\langle\phi_m|[G(E)^* - G(E)]|\phi_n\rangle \\ &= \frac{i}{2}[\langle\phi_m|G(E)^*|\phi_n\rangle - \langle\phi_m|G(E)|\phi_n\rangle] \\ &= \frac{i}{2}[\langle\phi_n|G(E)|\phi_m\rangle^* - \langle\phi_m|G(E)|\phi_n\rangle] \qquad (18) \end{aligned}$$

and finally, the sum leading up to $N(E)$ as in eq 16. The advantage with this approach is that the iterative linear solver normally converges faster than the Lanczos eigenstate approach. The drawback is that we need to compute the matrix elements explicitly for a possibly large number of flux vectors $|\phi_n\rangle$. In addition, the procedure has to be repeated for each energy, although this can in part be overcome by using a shifted-QMR.[19,20] From a computational point of view we need to identify the vectors $|\phi_n\rangle$ that have a nonnegligible contribution to the final result and include only those in the sum (eq 16).

IV. Numerical Experiments

The collinear $H + H_2$ exchange reaction, discretized using pseudospectral methods and smooth exterior scaling,[21] was used as a test problem. This is an optimal choice because it allows us to implement the computational methods and test them on a simple but nontrivial problem. Normal coordinates $(\mathbf{q_1},\mathbf{q_2})$ were used, and the dividing surface was chosen to be located at $f(\mathbf{q_2}) = 0$. The flux operator is then given as $F = I_1 \otimes F_2$[11,13] and the flux eigenstates can be obtained by diagonalizing a one-dimensional matrix F_2.

For the Lanczos approach (eq 17), we first investigated if a start vector can be found that minimizes the number of iterations. Full re-orthogonalization was used to bypass effects due to numerical round-off effects. A number of different choices of start vectors were tested with similar results: sum of flux vectors, random vectors, Gaussian wave packets, and transition state eigenstates. The reaction probability did not converge monotonically with the number of iterations, and the number of recursions needed was approximately equal to the size of the original matrix. The results for a start vector as a sum of flux vectors are shown in Figure 1. If one regards the method of eq 17 as a factorization, this indicates that there is no subspace of H that contributes significantly more to the final result than any other. The gain, which should not be underestimated, is that we have generated a tridiagonal matrix that it is possible to diagonalize. If we do not explicitly orthogonalize the Lanczos vectors, there will be a loss of orthogonality already after 30−50 iterations. Multiple copies of extreme eigenstates will show up as well as spurious states. This has the effect that the convergence of $N(E)$ slows down considerably and $M \gg N$ will be needed. This is somewhat worrisome because this is the approach that must be used for large systems. This could imply that the Lanczos scheme, in this formulation, is not optimal. These findings call for further investigations and comparison with, e.g., Chebychev polynomials.

For the Greens function approach (eq 16), two questions have to be considered: how many flux vectors do we need to include in the sum (eq 16) and which convergence tolerance is needed for the iterative solver. Here the QMR method[16,17] with a diagonal preconditioner was used. In Figure 2 we display the error of $N(E)$ as a function of the error tolerance $10^{-\epsilon}$ in the QMR. As is seen, the error in $N(E)$ decays linearly with the error tolerance for the QMR. A second question is how many

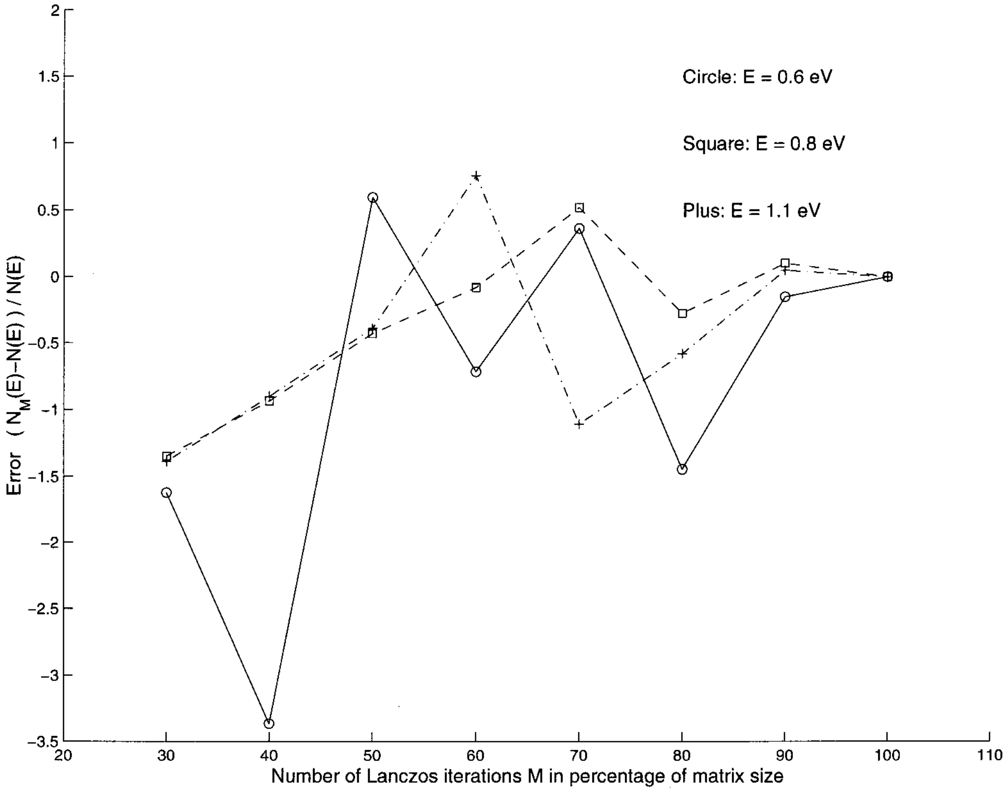

Figure 1. Convergence of $N(E)$ as a function of Lanczos recursions. The relative error after M Lanczos iterations is given as $(N_M(E) - N(E))/N(E)$.

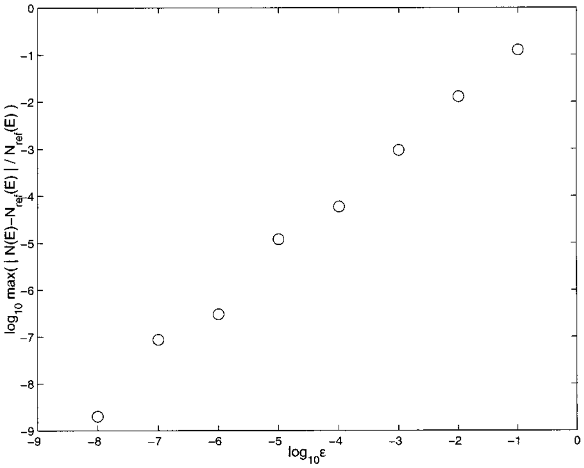

Figure 2. Convergence of $N(E)$ as a function of the tolerance $10^{-\epsilon}$ used for the linear solver, the quasiminimal residual method (QMR).

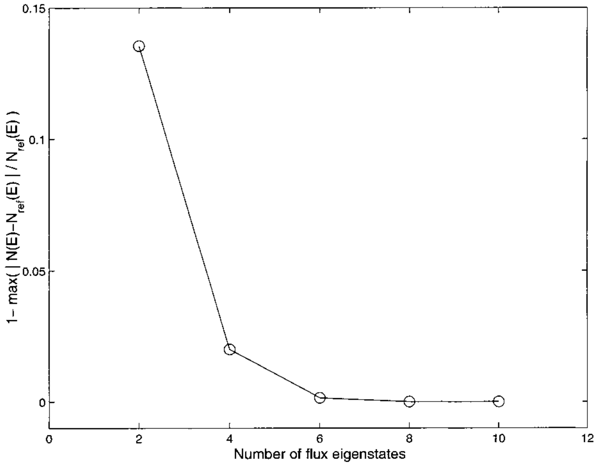

Figure 3. Convergence of $N(E)$ with respect to the number of eigenstates to the 1-dimensional flux operator.

flux eigenstates are needed to reach convergence. First we consider the number of states in the perpendicular degree of freedom. The flux vectors were selected according to a cutoff criteria. Only states with $V(q_1,q_2 = 0) \le V_c$, where $V(q_1,q_2)$ is the potential energy surface, were included. This has the effect of locating the flux states in the transition state region. For $V_c = 2$ eV, the error was on the order of 2%, for $V_c = 1.5$ eV it increased to 4%, whereas for $V_c = 1.0$ eV it was over 10%. The flux operator used here (eq 14) has a low rank with eigenvalues decaying (nearly) exponentially. In Figure 3 we show the convergence of $N(E)$ when the number of eigenstates (to the 1-dimensional flux operator) included in the sum is varied. It is clear that we need to include at least six flux eigenstates in the sum. For a system with a high density of states in the perpendicular degree of freedom, this might still lead to a large number of flux eigenstates, increasing the computational cost.

V. Discussion

To compute correlation functions for realistic systems, one must be able to handle functions of large Hamiltonian matrices. In this paper we have investigated the use of Krylov subspace methods, especially the Lanczos algorithm, to reduce the effective problem size. An important reduction of the computational effort was the finding by Mandelshtam[3] and Chen and Guo[4] that all correlation functions can be computed from a single recursion, a result that was used here to compute cumulative reaction probabilities. We found that the number of Lanczos iterations needed for convergence was on the order of the original matrix, although producing a tridiagonal matrix that can be diagonalized. If Lanczos recursions are used without explicit re-orthogonalization, the generated vectors quickly lost orthogonality and a large number of recursions were needed. We also noted that $N(E)$ could be computed by solving a number of linear systems $|\phi_n(E)\rangle = ImG(E)|\phi_n\rangle$. The linear solver converged faster than the Lanczos method discussed above, due to the minimization property. However, a large number of systems must be solved for each energy leading to a much higher computational cost.

It should be noted that the methods put forward here also can be used for time-dependent problems. The thermal rate constant can be expressed as a time integral of the flux-flux autocorrelation function[8]

$$k(T) = Q^{-1} \int \mathrm{d}t\, C(t) \tag{19}$$

$$C(t) = \mathrm{Tr}[\mathrm{e}^{-\beta H/2\hbar}\hat{F}\,\mathrm{e}^{-\beta H/2\hbar}\,\mathrm{e}^{i\hat{H}t/\hbar}\hat{F}\,\mathrm{e}^{-i\hat{H}t/\hbar}] \tag{20}$$

where Q is the reactant partition function. Wyatt,[22] within the RRGM formalism, did one of the first attempts to apply the Lanczos method to this problem. With $t_c = t - i\beta$ and $\beta = 1/kT$, the flux eigenstates formulation gives[1,10−12]

$$C(t) = \sum_n\sum_m \lambda_n\lambda_m|\langle\phi_m|\,\mathrm{e}^{-iHt_c/\hbar}|\phi_n\rangle|^2 \tag{21}$$

Using a recursively generated basis as above we can write

$$C(t) = \sum_n\sum_m \lambda_n\lambda_m|\langle\phi_m|VS\,\mathrm{e}^{-i\Lambda t_c/\hbar}S^{\dagger}V^{\dagger}|\phi_n\rangle|^2 \tag{22}$$

with advantages and disadvantages similar to eq 17. The correlation function can also be computed from a short time propagator

$$C(t) = \sum_n\sum_m \lambda_n\lambda_m|\langle\phi_m|\phi_n(t_c)\rangle|^2 \tag{23}$$

where the time stepping is given by

$$|\phi_n(T+\Delta t)\rangle = \mathrm{e}^{-iH\Delta t/\hbar}|\phi_n(t)\rangle = VS\,\mathrm{e}^{-i\Lambda\Delta t/\hbar}S^{\dagger}V^{\dagger}|\phi_n(t)\rangle \tag{24}$$

The difference from the short iterative Lanczos (SIL) method[23] is that an arbitrary initial state can be used here to propagate *all* $|\phi_n\rangle$ *at once*. The choice of start vector will affect the number of Lanczos iterations and thus the maximum time step Δt that can be taken. These ideas will be investigated in a forthcoming paper.

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