Journal of Theoretical and Computational Chemistry, Vol. 2, No. 4 (2003) 1–9

World Scientific
www.worldscientific.com

ON HARMONIC INVERSION OF CROSS-CORRELATION FUNCTIONS BY THE FILTER DIAGONALIZATION METHOD

VLADIMIR A. MANDELSHTAM
Chemistry Department, University of California, Irvine, CA 92697-2025, USA
mandelsh@uci.edu

Received

Harmonic inversion of Chebyshev correlation and cross-correlation functions by the filter diagonalization method (FDM) is one of the most efficient ways to accurately compute the complex spectra of low dimensional quantum molecular systems. This explains the growing popularity of the FDM in the past several years. Some of its most attractive features are the predictable convergence properties and the lack of adjusting parameters. These issues however are often misunderstood and mystified. We discuss the questions relevant to the optimal choices for the FDM parameters, such as the window size and the number of basis functions. We also demonstrate that the cross-correlation approach (using multiple initial states) is significantly more effective than the conventional autocorrelation approach (single initial state) for the common case of a non-uniform eigenvalue distribution.

Keywords:

1. Introductory Remarks

In this paper we are concerned with the solution of the eigenvalue problem

$$H\Upsilon_k = E_k\Upsilon_k \tag{1}$$

by the filter diagonalization method (FDM).

The main idea of the method is to reduce the possibly very large $K \times K$ eigenvalue problem to a small generalized eigenvalue problem

$$\mathbf{HB}_k = E_k\mathbf{SB}_k \tag{2}$$

for a specific small energy interval using, for example, a Fourier filtered basis defined by[1,2]

$$\psi(\varepsilon_j) = \int_0^T g(t)e^{i(\varepsilon_j - H)t}\phi dt \quad (j = 1, \ldots, J) \tag{3}$$

with some general initial state ϕ. Here we assumed that the propagation of the wavepacket $\phi(t) = e^{-itH}\phi$ was done up to time T; $g(t)$ is a weighting function to be specified later; the values ε_j defining the Fourier basis functions are uniformly distributed in the chosen energy interval.

The work by Wall and Neuhauser (W&N)[3] may be considered as conceptually most important publication on FDM, although it utilized the already known idea of a small subspace diagonalization.[1,2] However, while the previous implementations required the explicit construction of the filtered basis to evaluate the Hamiltonian and overlap matrices,

$$\mathbf{H}_{ij} = \psi(\varepsilon_i)^{\mathrm{T}}H\psi(\varepsilon_j)\,; \quad \mathbf{S}_{ij} = \psi(\varepsilon_i)^{\mathrm{T}}\psi(\varepsilon_j)\,, \tag{4}$$

W&N showed that for a special choice of $g(t)$ both $\mathbf{H}$ and $\mathbf{S}$ could be computed directly from the time autocorrelation function

$$C(t) := \phi^{\mathrm{T}}e^{-itH}\phi\,. \tag{5}$$

This led to even more appealing statement that reduction of the eigenvalue problem (1) to the harmonic inversion of the time autocorelation function

$$C(t) = \sum_k^K d_k e^{-itE_k} \tag{6}$$

with unknowns E_k and d_k is not only convenient but may also result in an efficient numerical algorithm. To be fair, the idea of solving the harmonic inversion problem was known, for example, in the framework of the Prony method,[4] which uses pure linear algebra avoiding either a nonlinear least squares fit or the low-resolution Fourier spectral analysis. The really key result of W&N was for a given time signal $C(t)$ start with the assumption (5) and formulate FDM in a way that led to a method of solving (6) by a *small* matrix diagonalization (rather than by solution of a large linear system followed by finding the roots of a high order polynomial as encountered in the original Prony algorithm).

However, the algorithmic implementation of FDM by W&N was not very efficient for the following reasons: The algorithm was formulated assuming the availability of the autocorrelation function for continuous time argument. The use of the Gaussian weighting function $g(t)$ lead to very elegant final expressions, which turned out to be inefficient numerically. With this choice, the matrix elements of the Hamiltonian and overlap matrices formally require evaluation of Fourier integrals of $C(t)$ and $dC(t)/dt$ from $-\infty$ to $+\infty$, which practically could only be evaluated approximately by truncation and discretization.

The key contributions of Refs. 5 and 6 by Mandelshtam and Taylor (M&T) were the following.

(a) Reformulating the FDM for the practical case of time signals available only at discrete and evenly spaced time points, thus replacing the Fourier integrals by finite Fourier sums and allowing one to exactly evaluate the corresponding matrix elements.

(b) Reduction of the harmonic inversion problem to the eigenvalue problem for the evolution operator $U := \exp(-i\tau H)$ (instead of H), thus eliminating the need in the time derivative of the signal.

(c) Implementing the most simple rectangular Fourier weighting function and recognizing the fact that it is numerically most efficient. This also eliminated the ambiguity in the choice of the weighting function.

(d) Establishing a simple prescription for the density of the Fourier basis functions, thus making the signal length the only parameter of the method.

(e) Recognizing the fact that the harmonic inversion problem could be solved directly for the Chebyshev autocorrelation function. This eliminated the unnecessary reference to the true time.

To be fair the latter idea was explicitly or implicitly explored in several other publications.[7–10]

We note that the M&T version of FDM is now routinely used by various groups. However, the issues related to items (c), (d) and (e) above still create some confusion in the literature. In the present paper, well clear this confusion as well as we discuss another interesting "twist" of FDM related to the use of the cross-correlation functions (instead of the autocorrelation). The idea of the latter, first introduced by W&N[3] and then extensively explored in Refs. 11–15, is reminiscent to that of the block-Lanczos algorithm.[16] The convergence of FDM for nearly degenerate eigenvalues may be noticeably slower than for the rest of the spectrum (see, e.g., the numerical demonstration in Ref. 17). The convergence may be facilitated by using $L > 1$ initial vectors ϕ_α to generate a time-dependent $L \times L$ cross-correlation matrix,

$$C_{\alpha\beta}(t) = \phi_\alpha^{\mathrm{T}} e^{-itH} \phi_\beta \,, \tag{7}$$

followed by its harmonic inversion,

$$C_{\alpha\beta}(t) = \sum_k b_{k\alpha} b_{k\beta} e^{-itE_k} \tag{8}$$

with unknowns E_k, $b_{k\alpha}$ and $b_{k\beta}$. The use of Eqs. (7) and (8) may also be advantageous in the cases of rapidly decaying signals (broad resonances[11]) or rapid loss of accuracy as time increases (e.g., semiclassical quantization[12,14]), etc. However, in this paper we are not concerned with the latter cases.

Simple arguments[13] show that propagation of L initial states increases the information content (per unknown) of a single signal point by a factor of L, while increasing the work for the matrix-vector multiplications by exactly the same factor L. In addition, the cross-correlation approach has an overhead (more inner products have to be computed at each time step and more vectors have to be stored in the core memory) relative to the autocorrelation approach. It is likely that for a uniform distribution of eigenvalues the cross-correlation approach would not be advantageous, while it may be useful in the cases of very non-uniform distribution of the eigenvalues, despite the overhead. This last conjecture will be tested in the present paper. To simplify our analysis we consider a bound quantum system, but expect that our conclusions will hold for a more general case of a quantum scattering problem.

2. Weighting Function versus No Weighting Function

The weighting function $g(t)$ in Eq. (3) must be specified. The most simple choice corresponds to the rectangular window[5,6]

$$\psi(\varepsilon) = \int_0^T e^{i(\varepsilon - H)t}\phi dt \tag{9}$$

where to simplify the presentation we consider the continuous time formulation. In the versions of FDM that require the explicit construction of the Fourier filtered basis functions $\psi(\varepsilon_j)$ this choice is most convenient as it allows one to continue the propagation further in time without wasting the previous calculations.

Another point is that in the low storage version of FDM the cpu-time to construct the small $J \times J$ matrices scales as NJ when the rectangular weighting function is used,[5,6] where $N = T/\tau$ is the number of time steps. For a general weighting function (see, e.g., expressions derived in Refs. 18–20) the cpu-time scales as NJ^2, which for a large problem with $J \sim 100$ and $N \sim 10^6$ time steps may become noticeably slow.

The use of the rectangular weighting function is usually out of question for the cases when the Fourier spectrum is to be estimated by a truncated Fourier integral (sum). The lack of apodization (a smoothly decaying weighting function) leads to the so-called truncation artifacts in the estimated spectrum, such as sinc-wiggles coming from the large peaks and obscuring the small peaks.

However, as long as the diagonalization step provides accurate eigenvalues the filtered basis functions do not have to "look nice". Although this statement may not be consistent with one's intuition, it is the fact, established by our multiple numerical tests comparing various weighting functions (see also Ref. 17), including exponential, cosine and gaussian forms. The conclusion is that as long as the weighting function does not truncate the signal (as the gaussian weighting), the results are not sensitive to it. This, in particular, suggests that the "truncation artifacts" in Eq. (9) are irrelevant for the convergence of the eigenvalues. If, in spite of these arguments, one still wants to use a smoothly decaying weighting function $g(t)$, but retain the optimal NJ numerical scaling for the matrix construction, one can follow the suggestion of Ref. 21: Essentially any reasonable weighting function $g(t)$ can be approximated by exponential or trigonometric functions. The simplest choice is given by the decaying exponential:

$$\psi_\gamma(\varepsilon) = \int_0^T e^{-\gamma t} e^{i(\varepsilon - H)t}\phi dt\,. \tag{10}$$

If for an operator A we define

$$A(\varepsilon, \varepsilon') := \psi(\varepsilon)^{\mathrm{T}} A \psi(\varepsilon')$$

since $\psi_\gamma(\varepsilon) = \psi(\varepsilon + i\gamma)$ we have

$$\psi_\gamma(\varepsilon)^{\mathrm{T}} A \psi_{\gamma'}(\varepsilon') = A(\varepsilon + i\gamma, \varepsilon' + i\gamma')\,.$$

That is, the use of an exponential weighting is very easy to implement by simply shifting all the real values ε_j to the complex plane. For large γ the exponential weighting effectively truncates the time signal and makes the results worth. Note, however, that the exponential weighting can be used in a non-uniform fashion, i.e., we can define the filtered basis by using the j-dependent γ:

$$\psi_j = \psi(\varepsilon_j + i\gamma_j)$$

with $\gamma_j = 0$ inside some small energy window and $\gamma_j > 0$, outside. With this construction the values ε_j are dense inside the window and sparse, outside. Such multiscale basis may be useful for special cases of *noisy* data with large dynamic range of amplitudes and widths,[22] however, it would hardly make any difference for noisless data (i.e., for the present case).

Another both convenient and simple choice corresponds to the cosine weighting[21]:

$$\psi_{\cos}(\varepsilon) = \int_0^T \cos(\delta t) e^{i(\varepsilon - H)t}\phi dt \tag{11}$$

with $\delta = \pi/2T$. Because $\psi_{\cos}(\varepsilon) = \frac{1}{2}[\psi(\varepsilon - \delta) + \psi(\varepsilon + \delta)]$ it is easy to see that calculation of the matrix elements in the cosine-weighted basis can be done using

$$\psi_{\cos}(\varepsilon)^{\mathrm{T}} A \psi_{\cos}(\varepsilon')$$
$$= \frac{1}{4}[A(\varepsilon-\delta,\varepsilon'-\delta)+A(\varepsilon-\delta,\varepsilon'+\delta)$$
$$+A(\varepsilon+\delta,\varepsilon'-\delta)+A(\varepsilon+\delta,\varepsilon'+\delta)]\,. \quad (12)$$

Clearly other types of the weighting functions using trigonometric/exponential forms could be handled similarly with the cpu-time scaling for the matrix construction as fast as with no weighting. At the same time, we see that at least with the cosine weighting the set of weighted basis functions is just some linear transformation of a non-weighted basis set. Therefore, the use of a weighted basis may hardly lead to more accurate eigenvalues than the use of a non-weighted one, subject to the correct choice for the basis density. The latter defined by the density of the values ε_j must be made according to the type of the weighting function used, the rectangular weighting function corresponding to a simple recipe (see below).

3. Harmonic Inversion of the Pseudo-Time Cross-Correlation Signal

Although written differently than before, the following equations are not new and as such are presented without derivation. The latter could be found in Refs. 6 and 13.

Let $\Phi_0 \in \mathbf{R}^{K\times L}$ be a rectangular $K \times L$ matrix with L linearly independent column vectors $\Phi_{0\alpha} \in \mathbf{R}^K$, where typically $L \leq 10$. The coefficients of Φ_0 are most conveniently generated by a random number generator. The Chebyshev recursion relations can now be used to obtain the solution of the "pseudo-time Schrödinger equation":

$$\Phi_t = 2H\Phi_{t-1} - \Phi_{t-2} \quad (t=0,1,\ldots,M) \qquad (13)$$

with initial conditions corresponding to $\Phi_1 = H\Phi_0$. Here without loss of generality we assumed that the Hamiltonian matrix has its spectrum within interval $[-1;1]$.

The state vectors Φ_t $(t=0,1,\ldots,M)$ can be used to construct the $L \times L$ cross-correlation matrix Y_t for time values $t = 0,1,\ldots,2M$ using the well known doubling scheme:

$$Y_{2t+s} = 2\Phi_t^{\mathrm{T}}\Phi_{t+s} - \Phi_0^{\mathrm{T}}\Phi_s \qquad (14)$$

with $s = 0, 1$.

The harmonic inversion problem for the pseudo-time cross-correlation signal reads

$$Y_t = \sum_{k=1}^{K} b_k b_k^{\mathrm{T}} \cos(t\omega_k) \qquad (15)$$

with the unknown eigenfrequencies ω_k and vector-coefficients $b_k \in \mathbf{R}^L$ that are related to the eigenvalues and eigenvectors of H according to

$$E_k = \cos\omega_k\,; \quad b_k = \Phi^{\mathrm{T}}\Upsilon_k\,. \qquad (16)$$

In order to find the eigenenergies in a selected energy window $[E_{\min}; E_{\max}]$ an equidistant grid of real values φ_j $(j = 1,\ldots,J)$ in the frequency domain with $\varphi_j \in [\omega_{\min};\omega_{\max}]$ is chosen, where $\cos(\omega_{\min}) = E_{\max}$ and $\cos(\omega_{\max}) = E_{\min}$.

Assuming the symmetry $Y_t = Y_{-t}$ let

$$X_t^{(p)} := \frac{2-\delta_{t0}}{4}(Y_{t-p}+Y_{t+p})$$

with $t = 0,\ldots,2M-2$. Now for each pair (φ_i,φ_j) and $p = 0,1$ define the square $L \times L$ matrices:

$$T_{jj}^{(p)} = \sum_{t=0}^{2M-2} X_t^{(p)} \left\{ (2M-t-1)\cos(t\varphi_j) + \frac{\sin[(2M-t-1)\varphi_j]}{\sin(\varphi_j)} \right\}$$

and for $i \neq j$

$$T^{(p)}ij = \frac{R_j^{(p)}\cos[(M-1)\varphi_i] - R_i^{(p)}\cos[(M-1)\varphi_j]}{\cos(\varphi_i)-\cos(\varphi_j)} + \frac{F_i^{(p)}\cos(M\varphi_j) - F_j^{(p)}\cos(M\varphi_i)}{\cos(\varphi_i)-\cos(\varphi_j)}$$

where

$$F_j^{(p)} = \sum_{t=0}^{2M-2} X_t^{(p)} \cos[(M-t-1)\varphi_j]\,,$$

$$R_j^{(p)} = \sum_{t=0}^{2M-2} X_t^{(p)} \cos[(M-t)\varphi_j]$$

The $K_{\text{win}} \times K_{\text{win}}$ matrices $\mathbf{S}$ and $\mathbf{H}$ with $K_{\text{win}} = JL$ are now given by

$$\mathbf{S} = \begin{pmatrix} T_{11}^{(0)} & \cdots & T_{1J}^{(0)} \\ \vdots & \ddots & \\ T_{J1}^{(0)} & \cdots & T_{JJ}^{(0)} \end{pmatrix}; \quad \mathbf{H} = \begin{pmatrix} T_{11}^{(1)} & \cdots & T_{1J}^{(1)} \\ \vdots & \ddots & \\ T_{J1}^{(1)} & \cdots & T_{JJ}^{(1)} \end{pmatrix} \qquad (17)$$

The eigenvalues E_k from the specified energy region can be estimated by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{B}_k = E_k \mathbf{S}\mathbf{B}_k \tag{18}$$

and the vector-coefficients b_k by

$$b_k = (\mathbf{B}_k^{\mathrm{T}} \mathbf{S}\mathbf{B}_k)^{-1/2} \mathbf{A}\mathbf{B}_k \,, \tag{19}$$

where the $L \times K_{\mathrm{win}}$ matrix

$$\mathbf{A} := (A_1, \ldots, A_J)$$

is constructed by stacking together the square $L \times L$ matrices

$$A_j = \sum_{t=0}^{M-1} (2 - \delta_{t0}) Y_t \cos(t\varphi_j) \,.$$

4. Low Storage FDM versus Explicit Basis Set Construction

To describe the dynamics of a quantum system it is often sufficient to restrict the calculation to computation of the eigenvalues E_k and projections $b_{k\alpha}$ of the eigenvectors Υ_k to specific states Φ_α. The E_k and $b_{k\alpha}$ can be readily obtained by solving the harmonic inversion problem (15), where one can use the states Φ_α as starting vectors in the pseudo-time propagation (13). As an example this strategy may be very suitable for the S-matrix computation.[13,15,23,24] However, if one still wants to have the eigenvectors explicitly, the FDM can be used for this purpose as well. Clearly, one can follow the original approach where the Fourier filtered basis for a specified energy window is generated explicitly by using

$$\Psi_{j\alpha} = \sum_{t=0}^{M-1} (2 - \delta_{t0}) \cos(t\varphi_j) \Phi_{t\alpha}$$

with $j = 1, \ldots, J$ and $\alpha = 1, \ldots, L$. The $\mathbf{H}$ and $\mathbf{S}$ matrices are then computed by

$$\mathbf{H}_{i\alpha,j\beta} = \Psi_{i\alpha}^{\mathrm{T}} H \Psi_{j\beta} \,; \quad \mathbf{S}_{i\alpha,j\beta} = \Psi_{i\alpha}^{\mathrm{T}} \Psi_{j\beta}$$

rather than by Eq. (17). The solution of (18) for $\mathbf{B}_k$ can be used to construct the eigenvectors:

$$\Upsilon_k = \sum_{j=1}^{J} \sum_{\alpha=1}^{L} \mathbf{B}_{k,j\alpha} \Psi_{j\alpha} \,.$$

However, this strategy requires one to specify in advance the values φ_j which may or may not correspond to the optimal choice (see next section) as generally the number M of Chebyshev terms needed for convergence is not known in advance, while J must be chosen according to M. Generally this approach requires several test runs before the optimal parameters are identified. Apparently, the same goal may be achieved more efficiently by first generating the pseudo-time signal Y_t and setting the harmonic inversion problem (15) as described in Sec. 3. In this case the window basis is specified after the main computational work is done. By varying the signal length and examining the convergence of the small generalized eigenvalue problem (18) for the eigenvalues in a specified region one can find optimal values of J and M for this region. To construct the desired eigenvectors the following formula can be used

$$\Upsilon_k = \sum_{t=0}^{M-1} \sum_{\alpha=1}^{L} a_{k,t\alpha} \Phi_{t\alpha}$$

where the coefficients are

$$a_{k,t\alpha} = \sum_{j=1}^{J} (2 - \delta_{t0}) \cos(t\varphi_j) \mathbf{B}_{k,j\alpha} \,.$$

Since the states $\Phi_{t\alpha}$ are only available "on-the-fly" the propagation must be repeated, but using the optimal propagation time M and minimal core memory (one array of size K per eigenvector to be constructed).

5. Practical Considerations: The Optimal Window Basis and Convergence

The total number of unknowns in the harmonic inversion problem (15) is $K(L+1)$. The signal matrix is symmetric $Y_t = Y_t^{\mathrm{T}}$, so the total number of independent algebraic equations in Eq. (15) (the total information content of the data) is $(2M+1)L(L+1)/2$. Thus, ideally all the eigenvalues may be determined by solution of Eq. (15) if the following condition for the total number of matrix-vector products N_{mv} holds:

$$N_{\mathrm{mv}} = ML \geq K \,. \tag{20}$$

That is, increase of L reduces M, but the total number of matrix-vector products needed to determine all the

K eigenvalues of H is independent of L! Of course one finds similar condition in the Lanczos or block-Lanczos algorithms.[16] However, taking into account the finite arithmetic and the fact that the harmonic inversion problem is solved locally in the frequency domain, this condition may be and often is violated in practice: the eigenvalues in the sparse regions of the spectrum require much less than K matrix-vector products, while those in the dense spectral regions may need many more than K products. It appears that in FDM the $N_{\rm mv}$ needed to converge a particular eigenvalue is rather simple function of the locally averaged density of states $\rho(E)$[6,13,25]:

$$N_{\rm mv}(E) \approx \pi\rho(E)\sqrt{1-E^2}\Delta H\,, \qquad (21)$$

where the spectral range of the Hamiltonian matrix ΔH is one here. The $\sqrt{1-E^2}$ factor arises from the frequency to energy mapping $E_k = \cos\omega_k$ leading to $\rho(\omega) = \sqrt{1-E^2}\rho(E)$. The corresponding condition in the frequency domain reads

$$N_{\rm mv}(\omega) \approx \pi\rho(\omega)\,. \qquad (22)$$

If the eigenfrequencies ω_k fill uniformly the $[0;\pi]$ interval the convergence for all ω_k is achieved simultaneously at $N_{\rm mv} \approx K$. However, for non-uniform case the "locally averaged density of states" defined as the number of eigenvalues in a small window devided by the window size is in principle ambiguous. (For example, it depends on the size of the "window".) As such, the optimal $N_{\rm mv}$ may deviate from the rough estimate (21) [or (22)] and will in particular depend on the size of the filtered basis and the precision used to implement the FDM algorithm. For example, we found that when the time signal is accurate to many significant figures, as in the present case of Chebyshev correlation functions, the use of quadruple precision for both the matrix construction and the solution of the corresponding ill-conditioned generalized eigenvalue problem may noticeably improve the convergence.

In order to achieve the performance of FDM according to the condition (22), it is important to choose the width of the spectral window, $\Delta\omega = |\omega_{\rm max} - \omega_{\rm min}|$ and the number J consistently with the propagation time M (half of the signal length). The best performance is achieved when the following condition is satisfied[5]:

$$J/\Delta\omega \geq M/\pi\,. \qquad (23)$$

The use of J much larger than needed to satisfy this inequality would result in unnecessarily large and very ill-conditioned matrices $\mathbf{H}$ and $\mathbf{S}$, which must be handled with great care. It is safe to use, e.g., $J/\Delta\omega = 1.1M/\pi$ if the resulting $K_{\rm win} = JL$ is not too small (e.g., $K_{\rm win} \sim 100$ corresponds to a reasonable choice). When for a particular M the eigenvalues are not converged, M is increased. As long as Eq. (23) holds, one has some flexibility in choosing the parameters J and $\Delta\omega$, e.g., one can keep J fixed and decrease $\Delta\omega$, or fix $\Delta\omega$ and increase J. It is also important to realize that, if condition (22) is nearly satisfied for a particular $M = M_0$, then increasing M substantially with Eq. (23) satisfied will result in very ill-conditioned generalized eigenvalue problem. Very often these aspects (especially in the cases of the explicit basis set construction) are ignored leading to misuse of the FDM. For example, the intuitively natural approach corresponding to the use of fixed values for J and $\Delta\omega$, while increasing M and looking for convergence, is very dangerous, because for too large values of M, when $J/\Delta\omega < M/\pi$, it may lead to poorly converged or even missing eigenvalues. This in turn may result in wrong conclusions about the performance of FDM.

6. Numerical Example

To compare the performance of FDM with single ($L = 1$) and multiple ($L > 1$) initial vectors, we use the benchmark test designed by Santra *et al.*[26] The corresponding test matrix is full but has only $K = 1000$ eigenvalues E_k, with 900 eigenvalues distributed randomly and uniformly in the interval $[-1;1]$ and 100 eigenvalues, in the interval $[-0.0005;0.0005]$. (In fact there are 101 eigenvalues in this interval, which is though unimportant.) Although here K is small, the very dense set of eigenvalues makes the FDM calculation very slow to converge according to the condition (21) giving

$$N_{\rm mv} \approx \pi\rho(0) \approx \pi 10^5 \approx 314,159\,. \qquad (24)$$

Notably, roughly the same number of matrix-vector products would be required if $K = 314,159$ eigenfrequencies ω_k were distributed uniformly in the interval $[0;\pi]$ which would result in the same density of states

$\rho(E) \approx 10^5$ for the eigenenergies $E_k = \cos(\omega_k)$ in the region of interest, $E \sim 0$. Another aspect complicating the analysis is that the dense island of 100 eigenvalues is isolated, so the "locally averaged density of states" is here very poorly defined. For example, the eigenvalues close to the edges of the island would need significantly smaller $N_{\rm mv}$ than those in the very middle of the island. Despite these arguments we decided to run FDM through this test, in particular, to demonstrate its superiority to the method of Santra *et al.*[26,27] named parallel filter diagonalization (PFD). The PFD uses a massive parallelization, a multiple wavepacket propagation with L of the order of 100, explicit filtered basis set construction and a Gaussian weighting function in Eq. (3) to construct the filtered basis. Among several obvious drawbacks the use of $J = 1$ (per wavepacket) resulting in very small total filtered basis with $K_{\rm win} = L$ is wasteful and makes the PFD especially inefficient. Nevertheless, based on their numerical tests the authors of Ref. 26 came to the conclusion that PFD (using $L = 120$ but $J = 1$ and implemented on 12 computers) is superior to their version of standard FDM (using $L = 1$ but $J = 120$ and only one computer) as the former needs by a factor of three less matrix-vector products $N_{\rm mv}/12 = 219,000$ *per computer* than the latter ($N_{\rm mv} = 620,000$)! Here we do not question the validity of this conclusion, but demonstrate that the present approach implemented without parallelization needs roughly twelve times less computers than the PFD to compute all the eigenvalues of interest to very high accuracy!

As in Ref. 26 our goal is to test the convergence for all the eigenvalues in the dense island as a function of $N_{\rm mv}$ and L. The eigenvalue is assumed to be well converged if the error is considerably less than the distance to the nearest eigenvalue. The errors are set to the differences between the exact and the computed eigenvalues. Note that in the FDM once an eigenvalue started to converge its error vanishes very rapidly with M (see, e.g., example in Ref. 5 or the following results).

To simplify our analysis for all the test calculations reported below, we set $K_{\rm win} = LJ = 150$ fixed to be able to get all the eigenvalues in the dense island at once. The energy window was placed symmetrically, $E_{\rm min} = -E_{\rm max}$, and its width was varied according to $\Delta\omega = \omega_{\rm max} - \omega_{\rm max} = M(\pi J)^{-1}$.

6.1. *Using a single initial vector* ($L = 1$)

Quite surprisingly the above estimate (24) turned to be nearly accurate as with $M = N_{\rm mv} = 314,159$ most of the eigenvalues are well converged. The corresponding eigenvalue errors are displayed in the upper panel of Fig. 1. The four eigenvalues marked with arrows are missing. Those typically have very close neighbors, i.e., are nearly degenerate. Convergence for all the eigenvalues could only be achieved with $M = N_{\rm mv} \approx 500,000$, which is notably greater than the predicted value for a uniform distribution of eigenvalues. This observation is consistent with that in Ref. 17. For the converged case most eigenvalue errors are extremely small, while for a few "stinkers" around $E = -0.0001$ the errors are by orders of magnitude larger. This region happens to be the most dense in the spectrum.

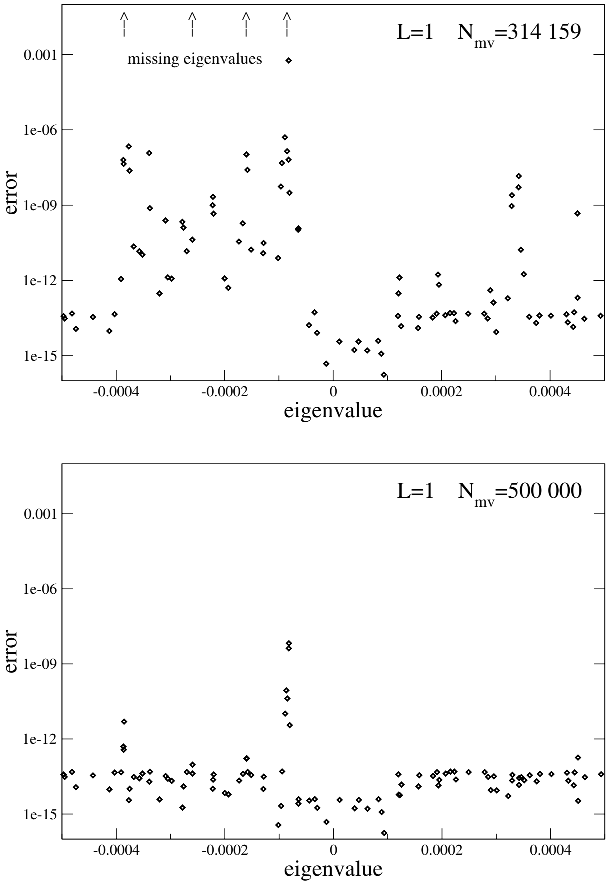

Fig. 1.

It is an interesting question how sensitive the error distribution is to the choice of the initial vector. Our tests show that $N_{\rm mv}$ needed to converge a particular eigenvalue to a certain high accuracy is generally insensitive (may vary only by a few percent) to the choice of the initial vector Φ_0, if the latter is generated randomly. For example, error distribution very similar to that shown in the lower panel of Fig. 1 is obtained using $L = 1$ and $N_{\rm mv} = 500,000$, but completely different Φ_0.

Note also that the present version of FDM with $L = 1$ significantly overperforms that used in Ref. 26 for the same matrix where $N_{\rm mv} \approx 620,000$ matrix-vector products were required to converge all the eigenvalues of question.

6.2. *Using multiple initial vectors* $(L > 1)$

Here we first report results using $L = 3$ initial states corresponding to a 3×3 cross-correlation matrix Y_t.

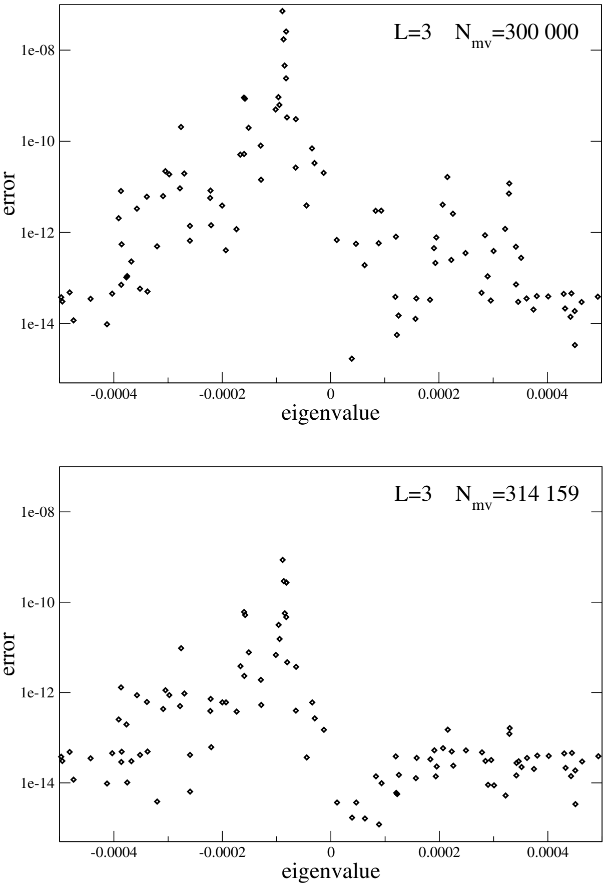

Fig. 2.

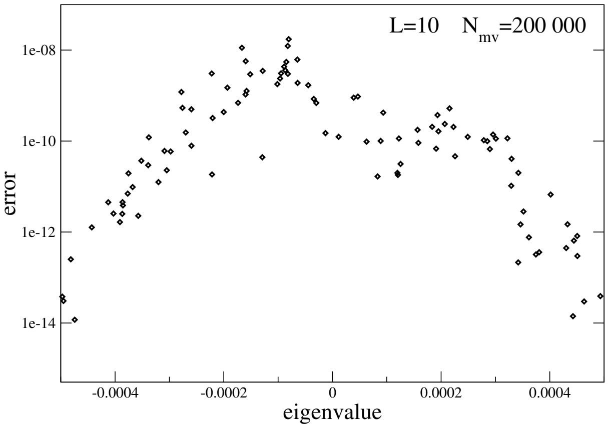

Fig. 3.

Interestingly, with $N_{\rm mv} = 314,159$ *all* the eigenvalues in the dense island are well converged (see Fig. 2)! The convergence is achieved even for $N_{\rm mv} = 300,000$, however, in this case the eigenvalue errors are notably larger. The increase of the overhead due to the need to compute nine inner products [Eq. (14)] rather than one and keep by a factor of three more vectors in the core memory is not high. The eigenvalue error is more uniform in the present case of $L = 3$ than for $L = 1$. This was also the case in the PFD calculations.[26]

The second test used $L = 10$, which corresponds to a significant increase of the core memory (factor of ten) and the cpu-time due to the $L^2 = 100$ inner products evaluated at each propagation step [Eq. (14)]. The latter may become comparable to the cpu-time of a single *sparse* matrix-vector product, although here the overhead is still small because the matrix is full. As seen in Fig. 3 *all* the eigenvalues are very well converged using only $N_{\rm mv} = 200,000$. The error distribution is much more uniform than for the cases of $L = 1$ and $L = 3$. Also, not surprisingly, the errors generally rapidly decrease toward the edges of the dense island, where the "local density of states" is smaller. (Quite unexpectedly, the reported eigenvalue errors in Ref. 26 are decreasing toward the edges of the island, which could probably be explained by not using an optimal filtered basis in the PFD.) Thus, here we used by a factor of twelve less computational resources than that required for the PFD to converge the same eigenvalues,[26] where $N_{\rm mv}/12 = 219,000$ and twice more core memory was used *per computer*!

However, most importantly, fewer matrix-vector products were needed using $L = 10$ than in both $L = 1$

and $L = 3$ cases, and even fewer than that predicted by our rough estimate (24). The explanation of the latter may be that the notion of the "locally averaged density of states" for an isolated dense eigenvalue island is not well defined.

To conclude, the cross-correlation version of FDM described in this paper using a few initial vectors with $L \leq 10$ is likely to be the method of choice for a large eigenvalue problem with non-uniform eigenvalue distribution. Our conclusions should also hold for the case of resonance calculation, where the propagation is carried out by a damped pseudo-time Schrödinger equation[28] rather than by Eq. (13).

Any fortran code used in this work is available from the author upon request.

Acknowledgments

The autor is an A.P. Sloan Research Fellow. This work was partially supported by the NSF, grant CHE-0108823. I am grateful to Robin Santra for providing data used for the numerical test.

References

1. M. Blanco and E.J. Heller, *J. Chem. Phys.* **83**, 1149 (1985); J.H. Frederick and E.J. Heller, *J. Chem. Phys.* **87**, 6592 (1987).
2. D. Neuhauser, *J. Chem. Phys.* **93**, 2611 (1990).
3. M.R. Wall and D. Neuhauser, *J. Chem. Phys.* **102**, 8011 (1995).
4. S.K. Gray, *J. Chem. Phys.* **96**, 6543 (1992).
5. V.A. Mandelshtam and H.S. Taylor, *J. Chem. Phys.* **106**, 5085 (1997).
6. V.A. Mandelshtam and H.S. Taylor, *J. Chem. Phys.* **107**, 6756 (1997).
7. C. Lanczos, *Applied Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1956).
8. W. Zhu, Y. Huang, D.J. Kouri, C. Chandler and D.K. Hoffman, *Chem. Phys. Lett.* **217**, 73 (1994).
9. V.A. Mandelshtam and H.S. Taylor, *J. Chem. Phys.* **102**, 7390 (1995).
10. R. Chen and H. Guo, *J. Chem. Phys.* **105**, 3569 (1996).
11. E. Narevicius, D. Neuhauser, H.J. Korsch and N. Moiseyev, *Chem. Phys. Lett.* **276**, 250 (1997).
12. V.A. Mandelshtam and M. Ovchinnikov, *J. Chem. Phys.* **108**, 9206 (1998).
13. V.A. Mandelshtam, *J. Chem. Phys.* **108**, 9999 (1998).
14. J. Main, K. Weibert, V.A. Mandelshtam and G. Wunner, *Phys. Rev.* **E60**, 1639 (1999).
15. V.A. Mandelshtam, *J. Phys. Chem.* **105**, 2764–2769 (2001).
16. J.K. Cullum and R.A. Willoughby, *Lanczos Algorithms for Large Symmetric Eigenvalue Computations* (Birkhäuser, Boston, 1985).
17. G. Barinovs and G. Nyman, *Chem. Phys.* **281**, 23 (2002).
18. R. Chen and H. Guo, *Chem. Phys. Lett.* **279**, 252 (1997).
19. M.H. Beck and H.-D. Meyer, *J. Chem. Phys.* **109**, 3730 (1998).
20. J.W. Pang, T. Dieckmann, J. Feigon and D. Neuhauser, *J. Chem. Phys.* **108**, 8360–8368 (1998).
21. H. Hu, Q.N. Van, V.A. Mandelshtam and A.J. Shaka, *J. Magn. Res.* **134**, 76–87 (1998).
22. J. Chen and V.A. Mandelshtam, *J. Chem. Phys.* **112**, 4429 (2000).
23. D.J. Tannor and D.E. Weeks, *J. Chem. Phys.* **98**, 3884 (1993).
24. D.J. Kouri, Y. Huang, W. Zhu and D.K. Hoffman, *J. Chem. Phys.* **100**, 3662 (1994).
25. V.A. Mandelshtam, T. Carrington, Jr., *Phys. Rev.* **E65**, 028701 (2002).
26. R. Santra and L.S. Cederbaum, *Phys. Rep.* **368**, 1 (2002).
27. R. Santra, J. Breidbach, J. Zobeley and L.S. Cederbaum, *J. Chem. Phys.* **112**, 9243 (2000).
28. V.A. Mandelshtam and A. Neumaier, *J. Theor. Comp. Chem.* **1**, 1 (2002).