

## LETTERS

### Anharmonic Vibrations via Filter Diagonalization of *ab Initio* Dynamics Trajectories

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Filter diagonalization (Wall, M. R.; Neuhauser, D. *J. Chem. Phys.* **1995**, *102*, 8011) is a new and efficient method for extracting frequencies and damping constants from a short-time segment of *any* time-dependent signal, whether of quantum nature or not. In this letter, we will demonstrate that filter diagonalization can be used to follow the anharmonic vibrational dynamics of Si<sub>6</sub>. Using the technique, we can locate (resolve) the normal modes (including the widths) from even a very short-time correlation signal generated by *ab initio* molecular dynamics calculations. Our results show that filter diagonalization can reduce significantly the necessary sampling time with an *ab initio* molecular simulation and aid in understanding normal-mode dynamics for systems that are affected by anharmonicity.

#### I. Introduction

It is extremely difficult experimentally to determine unequivocally the structure of gas-phase clusters. Various forms of rotation–vibration spectroscopy are perhaps the most definitive techniques for determining such definite structures.<sup>1–4</sup> Comparison of analytical models from *ab initio* calculations of the normal modes to experimental findings can reveal the structure of the cluster and its motions. This is not a trivial task, however, since the normal modes are determined experimentally at finite temperatures, whereas theoretically they would be conventionally calculated in terms of zero-temperature modes (i.e., the eigenvalues of the force-constant matrix). Instead, one would like a method that predicts finite temperature modes via proper extraction from the true evolution of the molecular system.

A promising technique for such a proper dynamical treatment is *ab initio* molecular dynamics (AIMD) simulation, which is emerging as a powerful tool to study molecular structure and dynamics. The advantages of the method are that it allows the

study of complex, many-dimensional systems, without the construction of a global potential energy surface, and at finite temperature. And, in addition to location of minima via *ab initio* simulated annealing, *ab initio* molecular dynamics also yields information on the finite temperature dynamics of the molecular system.<sup>5</sup> It is a very expensive technique, however, which has made it difficult in the past to extract spectra.

Normal-mode frequencies and line widths are typically extracted by a Fourier transform of the velocity auto-correlation function. Because of the CPU-intensive nature of AIMD and the fact that the Fourier transform<sup>6</sup> requires, for high resolution, very long simulation time,<sup>7</sup> this is a very expensive approach. Further, anharmonic effects can cause overlap of lines in the Fourier transform. This prevents the accurate extraction of spectral features.

In recent publications a new approach, filter diagonalization, was developed, which aims at extracting spectral information from a short-time signal. The method joins several other approaches for extracting information from a signal (MUSIC, maximum entropy or maximum pole and linear prediction, among others).<sup>8–10</sup> One attractive feature of filter diagonalization, however, is that it is suitable also for signals with a

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very large number of frequencies since it treats separately each small spectral range. Originally,<sup>11</sup> filter diagonalization was developed as a tool for accurate extraction of eigenstates in quantum systems (and from sparse matrices). The method was extensively developed and applied in that context.<sup>12–21</sup> Later it was generalized to be a method for extracting spectral information from a general signal.<sup>13</sup> In the new version, filter diagonalization was applied extensively to classical dynamics,<sup>22</sup> NMR studies,<sup>23,24</sup> and several challenging semiclassical quantization schemes<sup>25,26</sup> where recent works benefited from the introduction of a box filter leading to particularly simple equations.<sup>25</sup> The closest example to the work reported herein is a recent application to a rigid Lennard-Jones Ar<sub>256</sub> cluster where the method was demonstrated to be capable of extracting instantaneous normal-mode spectra,<sup>22</sup> and the density of states was extracted properly.

In this letter, we perform a more detailed study of the properties of the normal modes and their widths. We study the application of filter diagonalization to an ab initio dynamics simulation on a small, relative floppy cluster of Si<sub>6</sub>. We investigate the spectra and poles extracted with the method and show how the locations change with time. We also demonstrate that the normal-mode spectrum can be obtained even with times that are too short for a Fourier transform analysis. This is due to the fact that filter diagonalization uses a divide-and-conquer strategy to extract spectral information from any general signal. Specifically, eigenvalues outside the desired range are eliminated in the first stage by using the filtering basis, while eigenvalues within the range are extracted by diagonalization of small matrices. This illustrates the unique advantage to applying filter diagonalization to ab initio dynamics simulations to obtain spectra (i.e., minimizing the expense of an ab initio prediction of fully anharmonic vibrational frequencies). The normal modes extracted from filter diagonalization will be shown to be red-shifted (especially at low frequencies) from the modes found in the normal-mode analysis (i.e., direct diagonalization of the Hessian matrix) near the minimum configuration. This is due to bond softening at high amplitudes and shows the advantage of filter diagonalization, which allows the study of the true dynamical motions. Finally, in the Appendix, we further develop the theory to study matrix correlation functions.

## II. Filter Diagonalization Methodology

The methodology will be briefly reviewed here; a more complete coverage is available elsewhere.<sup>13,27</sup> The starting point is a signal,  $C(t)$ . In ab initio dynamics, this signal can be taken as the velocity autocorrelation function

$$C(t) = \sum_i \vec{v}_i(t) \cdot \vec{v}_i(0) \quad (1)$$

$\vec{v}_i$  in eq 1 correspond to the Cartesian components of the velocities for each Si atom. Note that in eq 1, in contrast to the usual definition of correlation function, we do not average over initial times. The first assumption is that we can write the signal as a sum of the damping terms

$$C(t) = \sum_j d_j e^{-i\omega_j t - \Gamma_j t/2} = \sum_j d_j e^{-i\Omega_j t} \quad (2)$$

with  $\Omega_j \equiv \omega_j - i\Gamma_j/2$ . Here the weights ( $d_j$ ), the frequencies ( $\omega_j$ ), and the damping factors ( $\Gamma_j$ ) are unknowns, as is the number of terms. (Rigorously  $C(t)$  will not be exactly given by eq 2, but the assumptions is reasonable even for a small molecule like Si<sub>6</sub>.)

Filter diagonalization then writes an artificial unknown “Hamiltonian”

$$H = \sum_j |\phi_j\rangle \Omega_j \langle \phi_j| \quad (3)$$

where at this stage the  $|\phi_j\rangle$  is an arbitrary real vector basis (it drops out of the final formulas, which only involve  $C(t)$ ). We also formally write an initial wave function

$$|\psi_0\rangle = \sum_j d_j^{1/2} |\phi_j\rangle \quad (4)$$

At the desired small frequency range,  $[\omega_{\text{bot}}, \omega_{\text{top}}]$ , we pick equispaced frequencies

$$\omega_l = \omega_{\text{bot}} + \delta\omega(l-1), \quad l = 1, 2, \dots, L \quad (5)$$

where  $\delta\omega = (\omega_{\text{top}} - \omega_{\text{bot}})/(L-1)$ .  $\delta\omega$  should be taken as the typical level spacing in the range (in practice, one should increase  $L$  until the results converge).

Using eq 5, we define a set of filtered functions,

$$\psi(\omega_l) = \int e^{i\omega_l t} \psi(t) g(t) dt \quad (6)$$

where  $g(t)$  is a filter function (a box function,  $g(t) = 1$  for  $0 \leq t \leq T$ , which was employed successfully by Mandelshtam and Taylor,<sup>15</sup> or the original Gaussian filter<sup>13</sup> are the most convenient choices, but a general filter function<sup>23</sup> can be used). The filtered functions serve as an energy-selected basis to the eigenfrequencies in the desired range, so that the eigenvalues  $\Omega_j$  can be extracted from diagonalizing  $H$  in this nonorthogonal set, i.e., by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{B} = \mathbf{S}\mathbf{B}\mathbf{\Omega} \quad (7)$$

where  $S_{kl} \equiv \langle \psi_k | \psi_l \rangle$  can be evaluated directly from the correlation function

$$S_{kl} = \int \int C(t+t') g(t) g(t') e^{i(\omega_k t + \omega_l t')} dt dt' \quad (8)$$

and similarly

$$H_{kl} = - \int \int C(t+t') i \frac{d}{dt} [g(t) g(t') e^{i(\omega_k t + \omega_l t')}] dt dt' \quad (9)$$

The emerging method is very simple: construct the matrices  $\mathbf{S}$  and  $\mathbf{H}$  from  $C(t)$  (eqs 8 and 9) and then solve eq 7. (The two-dimensional integrals in eqs 8 and 9 are easily converted to simple one-dimensional integrals, with negligible cost. For details, see refs 27, 23, 16). In addition, the weight is extracted from

$$d_j^{1/2} = \langle \psi(0) | \phi_j \rangle = \sum_l B_{lj} \int e^{iE_l t} f(t) C(t) dt \quad (10)$$

The method is numerically efficient since only a small number of terms is employed ( $L \approx 50-100$  even for each window even for spectra with a very large number of modes).

## III. Ab Initio Dynamics Methodology

To generate the velocities for the autocorrelation function we have performed an ab initio molecular dynamics (AIMD) simulation. By that we mean that the nuclei are treated as classical particles and are propagated according to Newton's equations of motion, whereas the electrons are treated quantum mechanically. All the forces on the nuclei are calculated as

the negative of the gradient of the Born–Oppenheimer (BO) potential energy surface (PES) for the electronic ground state of the system. At each time step along the trajectory the wave function is fully converged, which guarantees that the system always remains on the BO PES.

The test case here is the ground singlet state of the  $\text{Si}_6$  cluster. The electronic wave function is a restricted complete active space self-consistent field (r-CASSCF) wave function consisting of all configurations of the 24 valence electrons in 24 orbitals, with the restriction that only configurations with the zero open shells and a maximum of six excited electrons away from the dominant reference configuration are allowed. Total energy and gradient calculations were performed using the program HONDO,<sup>28</sup> which was modified to implement the open-shell restriction.<sup>29</sup> This modified HONDO program then was coupled to our molecular dynamics code as described in previous work.<sup>29–31</sup> Further details of the calibration of this wave function and its associated dynamics will be given elsewhere.<sup>29</sup>

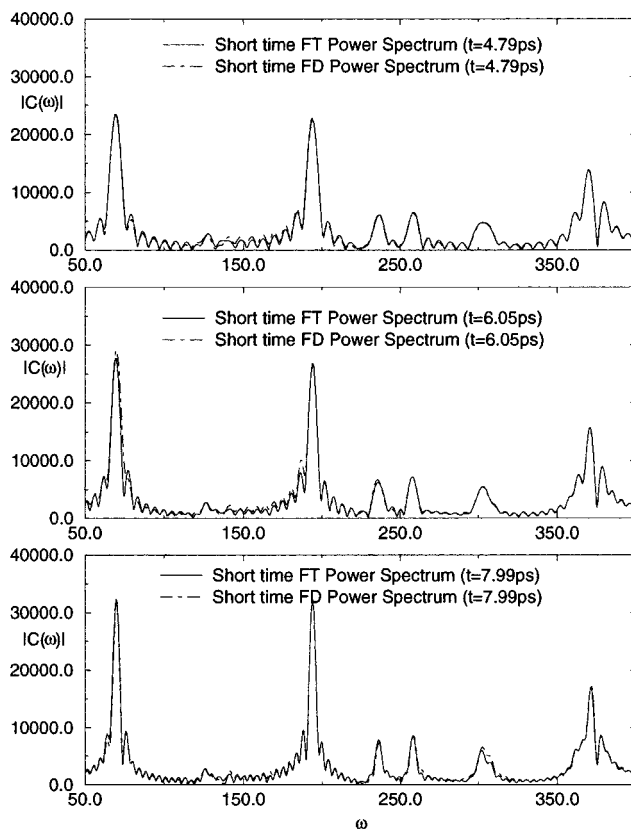
As AIMD is a computationally expensive (time-consuming) technique, we chose to use a valence double- $\zeta$  basis with the core electrons represented by an effective core potential.<sup>32</sup> Although we have shown<sup>29</sup> that the use of d-polarization functions is important both for the structure of the PES and its associated vibrational frequencies, we do not include them here. The main point of this paper is not to compare frequencies with experiment, but rather to show how filter diagonalization allows one to use shorter time correlation functions than required by the standard Fourier transform for obtaining frequencies. Given the expense of AIMD, this could have considerable impact on the length of AIMD trajectories carried out in the future.

At this level of approximation we have performed extensive simulated annealing calculations,<sup>29</sup> and we have determined that the ground-state structure for the  $\text{Si}_6$  cluster has  $C_2$  symmetry with no four atoms sharing the same plane. This geometry was chosen as the starting geometry for the simulation. The initial velocities were randomly chosen from a Boltzmann distribution at  $T = 30$  K and then adjusted to have zero total linear and angular momentum. We have used the velocity-Verlet algorithm<sup>33</sup> to integrate Newton’s equations with a time step of 100 au (2.42 fs), and the system was propagated for 3300 steps, a total of 7.99 ps.

#### IV. Results

Two different correlation functions were prepared with a time step of  $dt = 2.42$  fs. The first correlation function was constructed by calculating  $C(t) = \sum_j \vec{v}_j(t) \cdot \vec{v}_j(t_i=0)$ . The summation is over each component of the velocity for each atom. Again, we emphasize that unlike the regular definition of correlation function, here we did not average over the initial time, but rather held it fixed. A total of 3300 time steps was used. We first calculated a Fourier transform of the signal for different lengths of times, which does not resolve the poles due to overlapping poles (see Figure 1). Next we applied the filter diagonalization equations with the box filter (this filter was first suggested in this context in ref 16). Fifty filter functions were employed, and a frequency range of about 0.00015 au ( $\approx 33$   $\text{cm}^{-1}$ ) was sampled each time. The use of overlapping energy ranges enabled the verification of the accuracy of the eigenvalues. “Good” eigenvalues that appear in overlapping energy windows have very small intrinsic errors (see ref 13), in contrast to the spurious eigenvalues that are the result of the over-determinedness of the filter diagonalization equations.

Table 1 compares the extracted frequencies with the results from a normal-mode calculation<sup>34</sup> [i.e., direct diagonalization



**Figure 1.** Short-time FT (Fourier transform) power spectrum and the short-time FD (filter diagonalization) power spectrum for different lengths of times,  $t_{\text{max}}$  (see text). The correlation signal was calculated as  $C(t) = \sum_j \vec{v}_j(t) \cdot \vec{v}_j(t_i=0)$ , where  $j$  runs over all the components of the velocity for all atoms.

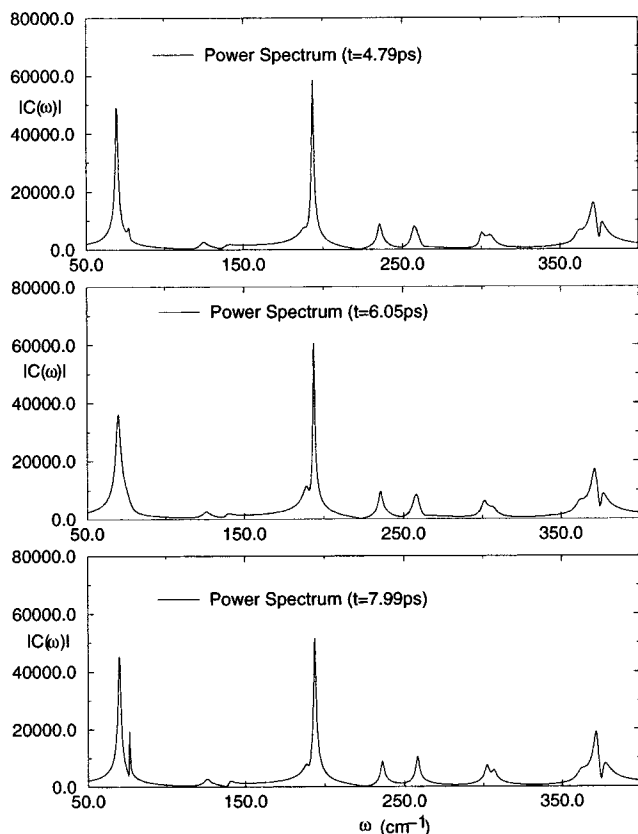
**TABLE 1: Extracted Eigenvalues from the ab Initio Molecular Dynamics Correlation Signal of  $\text{Si}_6$  by Using Filter Diagonalization with the Box Filter<sup>a</sup>**

7.99 ps			6.05 ps			4.79 ps			$\omega$ normal mode analysis
$\omega$	$\Gamma$	$ d_n $	$\omega$	$\Gamma$	$ d_n $	$\omega$	$\Gamma$	$ d_n $	
376.3	4.4	0.15	375.9	3.4	0.13	376.0	2.9	0.012	377.0
372.2	3.1	0.18	371.9	4.0	0.21	371.8	4.5	0.21	371.0
361.6	5.9	0.040	361.6	5.4	0.037	361.3	4.6	0.030	363.0
306.4	3.2	0.031	307.1	5.5	0.041	305.9	5.0	0.055	309.0
302.3	2.8	0.043	300.9	3.3	0.050	299.9	2.6	0.032	
258.2	2.1	0.048	259.7	6.0	0.30	260.8	4.5	0.031	264.0
			257.9	4.3	0.13	257.3	3.5	0.067	262.0
236.0	2.0	0.040	235.5	2.4	0.053	235.6	2.5	0.051	242.0
193.8	1.3	0.55	193.9	0.9	0.13	193.8	1.1	0.15	197.0
189.3	3.1	0.025	189.6	4.0	0.066	188.9	4.4	0.033	195.0
140.3	2.7	0.012	139.2	3.9	0.022	138.8	6.5	0.032	136.0
125.9	3.7	0.019	126.0	4.1	0.020	124.5	4.2	0.024	
76.6	0.1	0.011	76.0	7.1	0.064	77.3	1.1	0.009	87.0
70.0	1.5	0.16	69.8	2.9	0.24	69.6	1.4	0.16	86.0

<sup>a</sup> Results are shown for varying lengths of the correlation signal. The correlation signal is constructed by calculating  $C(\tau) = (1/T) \sum_{t=0}^T \vec{v}_j(t) \cdot \vec{v}_j(t+\tau)$ . Both the locations  $\omega$  and the widths  $\Gamma$  are in  $\text{cm}^{-1}$ .  $|d_n|$  are the absolute weights for the extracted frequencies.

of the numerical force-constant (Hessian) matrix]. The ab initio Hessian was constructed using finite differences of analytic gradients of the r-CASSCF energy.

For the purpose of graphical comparison to the analytic spectrum, we evaluated several expressions. First, we evaluated the direct Fourier transform, based on the available signal,  $\int_0^{\text{max}} C(t) e^{i\Omega t} dt$ . Next we evaluated the same expression, but under the assumption that  $C(t)$  has the form of eq 2, where the weights and frequencies are obtained from the filter diagonal-



**Figure 2.** Power spectrum (eq 12) from filter diagonalization for different sampled signal lengths. The correlation signal was calculated against as  $C(t) = \sum_j \vec{v}_j(t) \cdot \vec{v}_j(t_i=0)$ , and the spectrum was calculated from eq 12. The number of data points used to construct the spectrum for each figure is  $n_t = 1980, 2500,$  and  $3300$ , respectively.

ization procedure, leading to

$$C(\omega) = \int_0^{t_{\max}} C(t) e^{i\omega t} dt \equiv \sum_J d_J \frac{(e^{i(\omega - \Omega_J)t_{\max}} - 1)}{i(\omega - \Omega_J)}$$

The usefulness of this spectrum (which we label as short-time analytic spectrum) is that it can be compared directly to the direct Fourier transform. The good agreement of the two spectra, as demonstrated in Figure 1, shows both the validity of the assumption that  $C(t)$  can be represented in the form of eq 2 and the validity of the filter diagonalization procedure for extracting the spectral information.

While the short-time analytical spectrum is useful for verifying the validity of the filter diagonalization procedure, useful graphical information is obtained by setting  $t_{\max} = \infty$ , i.e., by using the obtained spectral weights to extrapolate the long-time behavior of the signal. The resulting spectrum (referred to below as the powerful spectrum) is calculated as

$$C(\omega) = \int_0^{\infty} C(t) e^{i\omega t} dt \quad (11)$$

which with the inherent assumption for the form of  $C(t)$  (eq 2) becomes

$$C(\omega) = \sum_J \frac{id_J}{\omega - \Omega_J} \quad (12)$$

The spectrum is shown in Figure 2 (using  $t_i = 0$ ). Although

we did not show it, the results are similar even for a shifted correlation signal (with  $t_i = 500$ ).

The spectrum in Figure 2 and Table 1 has several interesting features. First, the spectra show wide overlap of nearby frequencies (especially around  $300$  and  $375 \text{ cm}^{-1}$ ). Moreover, there is a distinct red-shift of low-frequency modes ( $\approx 10 \text{ cm}^{-1}$  for the  $70\text{--}80 \text{ cm}^{-1}$  mode). The spectra have several strong peaks and a few minor peaks that cannot be resolved in the direct Fourier transform but are easily resolved with filter diagonalization even for a very short time (with 1980 data points).

Another interesting aspect is the variation of the normal-mode frequencies, especially their widths, with the signal length. Table 1 shows specifically that the low- and intermediate-frequency modes change slowly, due to intermode coupling. They also show the variation of the normal-mode frequencies and their widths for the two different correlation functions. This indicates that at different times, different normal modes become the "dominant" (since the width represents the lifetime of the specific mode in the system) ones in the  $\text{Si}_6$  system. This is in agreement with the results obtained for the  $\text{Ar}_{256}$  cluster calculation.<sup>22</sup> Finally we note that the number of frequencies in the table is not always 12, the expected number of modes. There are at times 13 or 11 frequencies. The reason for the discrepancy is that the normal-modes picture is only approximate. The dynamics mixed the modes so that occasionally several modes mix together, and this dynamic is correlated, resulting in a single peak. Further, several modes have very small weight initially so that their effect is less pronounced. In addition, the appearance of extra spectral feature is probably due to overtone interaction (e.g., at  $140 \text{ cm}^{-1}$ ).

The fact that we can accurately represent the line widths ( $\Gamma_j$ ) of the normal modes introduces the question of whether these features that are due to intermode coupling can be used in dynamical studies. In this context, we note that in instantaneous normal-mode studies,<sup>35</sup> where frequencies are classified as purely real or purely imaginary, the purely imaginary normal modes were shown to be related to the diffusion behavior; an analogous treatment may be valid here.

## V. Conclusions

In conclusion, we have shown that filter diagonalization is an effective method for extracting normal-mode information from a short-time segment of the correlation function. These results should be of interest to those investigators concerned with identifying molecular structure via vibrational spectroscopy and to practitioners of molecular simulations. We have shown that the use of ab initio dynamics coupled with filter diagonalization is a promising way to extract frequencies and line widths without fitting a potential energy surface. Theorists should take note of the advantages of filter diagonalization over the Fourier transform, while experimentalists should recognize this coupling of techniques as a means to help identify different isomers of gaseous molecules and clusters.

As a final point, we note that in this work we used the velocity-velocity correlation function, while the relevant experimental quantity should be the dipole-dipole correlation in order to obtain correct intensities in addition to correct frequencies. In future studies we plan to use this form for more direct comparison to vibrational measurements; in practice, however, we expect similar features, e.g., red-shifting of peaks, since this is a feature which depends on the underlying dynamics of the normal modes.

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## VI. Appendix

In this paper, we employed filter diagonalization directly on the correlation function signal,  $C(t)$ . Here we outline an extension of this approach that can allow, in principle, the extraction of eigenvectors as well as eigenfrequencies.

We use now, in contrast to that in the paper, the initial time-averaged correlation function

$$\bar{C}_{ij}(t) = \int d\tau \langle v_i(\tau) \cdot v_j(t+\tau) \rangle$$

and assume that the normal-mode eigenvectors can be written as

$$\bar{v}(t) = \sum_n a_n e^{-i\Omega_n t} \bar{\zeta}_n$$

where the  $\bar{\zeta}_n$  are the normal-mode eigenvectors. For simplicity, in this derivation we assume that the normal-mode frequencies are purely real. (Extensions to imaginary frequencies will be presented in future publications.) It readily follows that

$$\bar{C}_{ij}(t) = \sum_n \sum_n |a_n^*| a_m e^{i\Omega_n \tau} e^{-i\Omega_m(t+\tau)} \zeta_{ni} \zeta_{nj}$$

(where  $\zeta_{ni}$  is the  $i$ th component of the  $n$ th eigenvector). If we assume that  $\langle e^{-i(\Omega_n - \Omega_m)\tau} \rangle = \delta_{nm}$ , it follows that

$$\bar{C}_{ij}(t) = \sum_n |a_n^2| \zeta_{ni} \zeta_{nj} e^{-i\Omega_n t}$$

Thus, by diagonalizing the filter diagonalization equation for a restricted set of  $i, j$ , we can find  $\zeta_{ni}$ . The use of filter diagonalization with many initial vectors was outlined in ref 13. Similarly, we can find the overlaps with a specific set of initial vectors,  $\bar{\eta}_k$ ;  $k = 1, \dots, K$ , containing any desired number of vectors ("K") and construct a set of matrix overlap functions

$$\bar{C}_{k,k'}(t) = \int d\tau \langle (\bar{\eta}_k \cdot \bar{v}(\tau)) (\bar{\eta}_{k'} \cdot \bar{v}(t+\tau)) \rangle$$

and use it to extract the overlaps,  $\bar{\zeta}_n \cdot \bar{\eta}_k$ . These overlaps could

be, for example, measuring the weight of the mode with respect to certain motions.

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