Vibrationally resolved spectra from short time quantum molecular dynamics by the Filter-Diagonalization method

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Abstract

The possibility of calculating vibrationally resolved spectra from very short numerically exact and approximate quantum dynamical propagations using the new Filter-Diagonalization method is explored. The benchmark process under study concerns electron photodetachment in the I^-Ar_2 complex. Comparison with results obtained from long time propagations and with experiment reveals the power of the Filter-Diagonalization scheme. Using the new methodology it now becomes possible to extract positions of spectral peaks for large polyatomic systems from approximate quantum propagations e.g., by means of the recently developed Classical Separable Potential approach.

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I. Introduction

The idea of calculating spectra from time-dependent wavepackets goes back to the works of Heller[1−3] some twenty years ago. The time-dependent method, based on converting the autocorrelation function into the spectrum via a Fourier transform represents in many cases a favorable alternative to the usual time-independent approach.[4] Within the time-dependent formulation a single wavepacket propagation is sufficient for obtaining the whole spectrum in contrast to the time-independent methods where the absorption cross-section has to be repeatedly evaluated for each energy. A thorough discussion about this subject with many examples can be found in the recent book by Schinke.[5]

The resolution of a spectrum obtained by Fourier transforming the autocorrelation function is of course inversely proportional to the length of the propagation. For direct or near-direct photodissociation processes and for multidimensional cases where relaxation to the 'bath' is fast lines are broad and short time propagation usually suffices. On the other hand, narrow lines corresponding long lived states created by a certain photochemical process require costly long time propagations. The situation is particularly critical for large polyatomic systems where numerically exact propagation is not possible and approximate quantum dynamical methods have to be employed. Due to their approximative nature these methods deteriorate in time and therefore do not allow for very long accurate simulations. Most of these approaches such as the Time-Dependent Self-Consistent Field (TDSCF) method[6−8] or the recently developed Classical Separable Potential (CSP) method[9] are based on the mode separability *ansatz* or go beyond it (Multiconfiguration TDSCF[10−15] or Configuration Interaction extension of CSP[16,17]). In this study we employ the CSP approach together with numerically exact propagations.

A general method for extracting positions of spectral peaks from very short time signals called Filter-Diagonalization (FD) has recently been proposed and successfully applied for extracting frequencies and widths of resonances.[18−21] The basic idea is to restrict the calculation to a narrow spectral range and to use the short time autocorrelation function for generating a good basis set for the peak positions and widths evaluation in the given range. In this paper, where a bound photochemical process is simulated, we apply the FD method not to extract resonances but stationary states which represents a challenge of its own right.

Although the CSP method is tailored for systems with up to 100-1000 atoms, we do not fully exploit the potential of the CSP approach here. Instead, in order to compare in this early study spectra obtained from approximate simulations to numerically exact propagations, we restrict ourselves to a small albeit realistic and experimentally relevant system. The process under study concerns the vibrational quantum dynamics following electron photodetachment in the I^-Ar_2 cluster as investigated using photoelectron and ZEKE spectroscopy in the group of Neumark[22,23] and using quantum propagations in our earlier studies.[9,17,24] The principal purpose of this work is to present a method for obtaining positions of spectral peaks from very short approximate or numerically exact propagations using Filter-Diagonalization, which opens new possibilities in spectra modeling of large systems.

The paper is organized as follows. In Section II we briefly review the new computational techniques and give details about the system under study. In Section III we present and discuss the results of the calculations and in Section IV we summarize the main achievements.

II. Method and System

A. Time-dependent approach to spectroscopy

In the seventies, Heller pioneered a time-dependent approach for the calculation of absorption (or photoelectron) spectra.[1−3] Within this scheme a wavepacket $\Psi(q_1, ..., q_N, t)$ is propagated for a sufficiently long time and the corresponding autocorrelation function $C_A(t) =< \Psi(q_1, ..., q_N, 0)|\Psi(q_1, ..., q_N, t) >$ is evaluated. The formula for the spectral intensity $I(\omega)$ then reads[3]

$$I(\omega) \sim \omega \times \int_{-\infty}^{\infty} C_A(t) e^{i(E_i+\omega)t} dt, \tag{1}$$

where E_i represents the initial energy.

The standard way to obtain the spectrum from the autocorrelation function is via the Fourier transform (e.g., using the Fast Fourier Transform (FFT)[25] algorithm). However, to achieve good spectral resolution the Fourier transform requires a sufficiently long propagation and there are many cases, especially involving polyatomic systems, where this is computationally excluded. For systems with more than four atoms numerically exact calculations become prohibitively costly and the separable methods, which are usually applied, are short time approximations which tend to deteriorate if propagation is carried for too long. The next subsection briefly describes a recently developed method for extracting the positions of the spectral peaks from very short propagations.

B. Filter-Diagonalization

The filter diagonalization method described in detail elsewhere[18–21] enables one to calculate the energy spectra of the system either only from the autocorrelation functions $C_A(t)$ or, in the case of several propagations from different initial wavefuctions, also from the cross-correlation functions $C_{nn'}$ (t),[21] where t<T. The key points are:

i) Propagation time T can be much shorter than the time which is required to get the energy spectra by FFT or by other known methods.

ii) There is no need to know what is the Hamiltonian for which the auto/cross correlation functions were calculated. The time evolution operator is represented by a matrix **U** which is constructed only from the knowledge of the auto/cross correlation functions.

iii) The energy (E) spectra of the system are obtained from solving a general eigenvalue problem

$$\mathbf{U}\Psi = \lambda \mathbf{S}\Psi, \tag{2}$$

where **U** and **S** are the time propagator and overlapping super-matrices, and $E = i(\Delta t)^{-1} ln\lambda$.[21]

The FD method also provides an error estimate (associated with the FD scheme itself and not with approximations in propagations in the case of CSP calculations) of the calculated spectra. The error is obtained by the diagonalization of the time evolution operator **U** calculated by the FD method at different times , $t = \Delta t, 2\Delta t, 3\Delta t$.[20,21] For bound systems where the eigenvalues E should have real values only, the imaginary parts of the calculated eigenalues E (i.e. the widths of the peaks) can be used as another error estimates of the results obtained by the FD method. In the present work we use the latter values as error estimates since they come out larger than the former values.

C. Classical separable potential method

Quantum propagations were performed both numerically exactly and using the recently developed CSP method, detailed description of which is given elsewhere.[9,16] Very briefly, the basic concept of the CSP approach lies in simplifying the multidimensional coupled quantum dynamical problem by constructing an effective time-dependent separable mean-field potential for each degree of freedom using auxiliary classical trajectories. With the use of this ensemble of trajectories, an effective potential for each mode is computed. Subsequently, a one-dimensional quantum propagation is performed for each mode using the above potentials.

The initial coordinates and momenta for the set of n_T classical trajectories $\{q_1^{(\alpha)}(t)$, $q_2^{(\alpha)}(t), ..., q_N^{(\alpha)}(t), \alpha = 1, ..., n_T\}$ are chosen such as to map the initial wavepacket using Husimi phase space distribution[26] corresponding to the initial quantum state of the system. A set of trajectories is then generated by solving the classical equations of motion. A separable time-dependent effective potential $V_j(q_j,t)$ for each mode j $(j = 1, 2, ..., N)$ is then constructed by averaging over all trajectories as follows:

$$V_j(q_j,t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_{j-1}^{(\alpha)}(t), q_j, q_{j+1}^{(\alpha)}(t), ..., q_N^{(\alpha)}(t))w_\alpha + \frac{1-N}{N}\overline{V}(t). \quad (3)$$

In the above equation, V is the fully coupled potential, N is the number of modes, and the summation runs over all MD trajectories and w_α is the Husimi weight of trajectory α. The time-dependent but coordinate-independent constant $\overline{V}$

$$\overline{V}(t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_{j-1}^{(\alpha)}(t), q_j^{(\alpha)}(t), q_{j+1}^{(\alpha)}(t), ..., q_N^{(\alpha)}(t))w_\alpha \quad (4)$$

does not influence the dynamics and only ensures that the single-mode potentials sum up approximately to the total potential energy.

Next, the time-dependent Schrödinger equation within the separable approximation is solved for each mode j

$$i\hbar\frac{\partial\psi_j(q_j,t)}{\partial t} = (\hat{T}_j + V_j(q_j,t))\psi_j(q_j,t), j = 1, ..., N. \tag{5}$$

Here, $2\pi\hbar$ represents the Planck's constant and $\hat{T}_j$ is the kinetic energy. Normal mode coordinates of the anionic species are used in this simulation. The total wavepacket for the system under study is finally given as a product of the single-mode wavefunctions

$$\Psi(q_1, ..., q_N, t) = \prod_{j=1}^{N} \psi_j(q_j, t). \tag{6}$$

D. System and Computational Details

The I^-Ar_2 complex has the shape of an isosceles (nearly equilateral) triangle.[23,24] In our simulations the ground state vibrational wavefunction is promoted upon electron photodetachment to the neutral I3/2 surface,[17,23] where it undergoes dynamical evolution. After electron photodetachment, the energy of the system is below the dissociation limit and consequently the atomic motions are bound. The anionic and neutral iodine-argon potentials were determined from ZEKE experiments.[22] In this work we use the same pair potential parameters as in our previous studies.[9,17,24]

The coordinates used in the quantum simulations were the three anionic normal modes - symmetric and asymmetric stretch, and the bending mode. The initial wavepacket was taken as product of corresponding harmonic eigenfunctions. A grid of 64 points for each degree of freedom proved to be sufficient. The CSP wavepackets were propagated using the split-operator technique[27] with a time-step of 0.65 fs. The numerically exact wavefunctions were propagated using the Chebyshev method[28] with a 6.5 fs time-step. In all simulations, the action of the kinetic energy operator was evaluated using the Fourier approach.[29] 200 classical trajectories, which provided converged classical separable potentials, were generated using a standard Gear routine[30]. For the Filter-Diagonalization calculations 50 basis functions provided well converged results in the interval -240 to -150 cm^{-1}, where zero corresponds to the energy of a fully dissociated neutral cluster.

III. Results and Discussion

Vibrational motions of individual modes on the neutral I3/2 surface of the IAr_2 complex have typical periods of motion around 1 ps. Therefore, quantum propagation for tens of picoseconds is necessary to extract the vibrationally resolved photoelectron spectrum using the standard Fourier transform method. Fig. 1 depicts the modulus of the numerically exact autocorrelation function on the interval 0 to 24 ps. A rather complicated pattern is observed which is dominated by a series of major recurrences spaced by 2-2.5 ps, among which more irregular small recurrences occur. This pattern gives us an information about the reappearences of the evolving wavepacket in the initial Franck-Condon region.

As discussed in the Introduction, large polyatomic systems, such as big atomic and molecular clusters, biomolecules, or condensed phases, to which most of the interest is directed, do not allow for numerically exact quantum dynamical description. Often, the quantitative accuracy of the approximate methods decays before a sufficient information for the Fourier transform of the autocorrelation function is gained. In Fig. 2 comparison is made between the short time numerically exact and CSP autocorrelation functions. While for about 500 fs CSP is an excellent quantitatively correct approach, an error slowly starts to build up afterwards. Clearly, we cannot expect CSP to provide accurate information about the whole 24 ps dynamics. Still, it gives a very reasonably description of the early dynamics till about 1200 fs.

Conversions of the long and short time autocorrelation functions into the spectral information is shown in a complex Fig. 3. Direct application of the FFT method to the long 24 ps numerically exact autocorrelation function yields the main peak with relative intensity of 1 at -231 cm^{-1} (with zero set at the energy of the fully dissociated neutral cluster). A tail to the blue with major peaks spaced by approximately 15 cm^{-1} and a few minor peaks is observed in a very good agreement with the ZEKE experiment.[23] As a matter of fact, the spectral resolution of 1.5 cm^{-1} which comes from Fourier transforming a finite time signal is better than that of the experimental spectrum.

Application of the Filter-Diagonalization method to the 24 ps autocorrelation function gives by far superior results than the above discussed FFT scheme in terms of spectral resolution. All the major peaks are perfectly sharp (the corresponding error bars in Fig. 3 form optically a single line) with spectral resolution being better than 0.001 cm^{-1}. Only the peaks in the very tail of the spectrum come out less sharp but still significantly better than the FFT ones. One of the practical consequences of this is that we can now resolve peaks which were earlier hidden within one relatively broad line, such as the three peaks around -185 cm^{-1} (see Fig. 3). Note that, unlike the sizes of the FFT peaks, the intensities of the FD peaks in Fig. 3 are purely arbitrary and their values are chosen such as to provide a clear picture.

In terms of future applications to much larger systems a crucial question arises about how much information can be extracted from a very short time propagation where separable approximations still hold well. The chosen short 1.2 ps time interval covers roughly one vibration of the individual modes and represents only a half way to the first major recurrence in the autocorrelation function. Not surprisingly, FFT for such a short time signal gives only a broad spectral envelope and is essentially useless (see Fig. 3). What might be more of a surprise is that a lot of spectral information is obtained using the FD approach. When applied to the short time numerically exact autocorrelation function it gives sharply the position of the main peak, and correctly, though much less sharply the second and one more peak. The non-negligible widths of the side peaks are consequences of the very uncomplete time information, nevertheless the positions of the peaks come out very well and the peaks are well resolved (the widths do not overlap).

Since within the FD approach we are not calculating spectral intensities it is possible to improve the short time results by performing propagations also from other initial vibrational states than the (experimental) ground vibrational state (denoted 000) on the anionic surface, or possibly even from an initial state which is a linear combination of the corresponding vibrational eigenstates. The additional propagations help in better exploring the configurational space and thus gaining more information within the short time dynamics. They also allow to evaluate cross-correlations which were shown to be helpful in extracting very broad resonances from short time propagations started from very delocalized initial wavepackets.[21] However, in the present work concerning a bound problem studied via propagations of initially rather localized wavefunctions the cross-correlations proved to be practically redundant and were not used.

In this study we performed additional numerically exact short time propagations started from the 111 and 222 harmonic initial states and used these to refine the previous results. The choice of these lower vibrational eigenstates was influenced by the fact that the CSP approximation, for which the numerically exact results serve as a benchmark, works best for localized initial states, which can be well represented by a moderate number of points from the Husimi phase space distribution. As can be seen on Fig. 3 we can now extract significantly more peaks. Also some of the old peaks (e.g., the second most intense peak) can now be determined more accurately and sharply.

Finally and most importantly, Fig. 3 shows that the approximate CSP short time propagation combined with the FD method gives results of comparable quality with the corresponding numerically exact calculation. Indeed, from a single short time autocorrelation function the same well resolved three peaks are extracted by the two dynamical methods. The error caused by the CSP approximation is small - the main peak becomes less sharp and the side peaks are less than 1 cm^{-1} off the short time numerically exact values and even slightly sharper. We note here that for better comparison all the CSP peaks depicted in Fig. 3 were shifted by 16.376 cm^{-1} which is the difference between the numerically exact and the approximate CSP total energies of the cluster after electron photodetachment. Adding more autocorrelation functions corresponding to propagations started from different initial wavefunctions has the same effect as in the case of numerically exact propagations. Three functions (000, 111, and 222, as before) allow to resolve already five peaks and adding four more functions (started from the 100, 200, 101, and 110 harmonic vibrational functions on the anionic surface) brings new spectral peaks and improves resolution of some of the existing ones.

IV. Conclusions

In the present study we showed how vibrationally resolved spectra can be extracted from quantum dynamical simulations of the electron photodetachment process in a small benchmark system - the I^-Ar_2 complex. From a long time numerically exact simulation, spectrum which is in a very good agreement with the ZEKE experiment is extracted using the standard FFT method. Filter-Diagonalizationd gives the same peak positions as the FFT method but with a grosly improved resolution. More importantly, the positions of the main peaks can be extracted using FD (but not FFT) also from a very short time propagation using numerically exact or approximate CSP methods, and they can be further refined by performing additional simulations started from different initial wavefunctions. The new results presented here are very encouraging and have far reaching consequencies for future simulations of large systems where numerically exact quantum dynamical calculations are not possible.

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Figure Captions

Figure 1: Absolute value of the autocorrelation function obtained from a long time numerically exact propagation.

Figure 2: Short time numerically exact and CSP autocorrelation functions.

Figure 3: Comparison between spectra obtained using FFT and Filter-Diagonalization for long and short time numerically exact and CSP propagations. Error bars indicate the precision of the Filter-Diagonalization method.