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Citation: The Journal of Chemical Physics **111**, 6168 (1999); doi: 10.1063/1.479920
View online: http://dx.doi.org/10.1063/1.479920
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/111/14?ver=pdfcov
Published by the AIP Publishing

On the scaling of semiclassical initial value methods

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(Received 27 May 1999; accepted 16 July 1999)

The semiclassical initial value method of Walton and Manolopoulos, the cellularized frozen Gaussian approximation for the calculation of bound–bound Franck–Condon spectra, has been applied to a series of model problems with up to ten coupled degrees of freedom. The number of classical trajectories required to converge these spectra is found to increase exponentially with the number of degrees of freedom in the model problems. On comparison with earlier applications of the method to the threshold photodetachment spectra of the Ar_nI^- $(n=2-6)$ anions, it appears that the number of trajectories required to converge a Franck–Condon spectrum semiclassically is directly proportional to the number of final quantum states which contribute to the spectrum. © *1999 American Institute of Physics.* [S0021-9606(99)02038-3]

A semiclassical initial value study[1] was reported recently on the Ar_nI^- $(n=2-6)$ threshold photodetachment spectra recorded by Neumark and co-workers.[2] The motivation behind the study was to show how an entirely second-order semiclassical initial value method could be applied to a series of realistic molecular bound-state problems that were both within and beyond the current range of more exact quantum dynamical calculations.

The semiclassical initial value method chosen for the Ar_nI^- photodetachment simulations—the cellularized frozen Gaussian approximation (CFGA) of Walton and Manolopoulos—was designed specifically for the calculation of bound–bound Franck–Condon spectra and can be derived[3] by combining the Herman–Kluk frozen Gaussian approximation[4] with Heller's cellular dynamics algorithm,[5] the latter of which can be viewed as a Filinov-smoothed[6] version of an initial value representation advocated in other contexts by Miller.[7] The CFGA provides a solution to the oscillatory integrand associated with the Herman–Kluk approximation, and is well suited to the study of multidimensional systems in which all relevant vibrational modes have similar frequencies, such as the Ar_nI^- clusters.[1]

In contrast, Ovchinnikov and Apkarian have used mixed-order initial value methods to simulate the electronic absorption spectra of halogen molecules imbedded in inert gas matrices.[8,9] In these instances, it is appropriate to carry out the semiclassical propagation of system and bath coordinates to different orders within the stationary phase approximation. For example,[9] the high-frequency quantum system (the halogen molecule) can be treated to second order with the Herman–Kluk frozen Gaussian approximation, while the low-frequency bath degrees of freedom (the inert gas matrix) can be treated to zeroth order with the original frozen Gaussian approximation.[10] This latter frozen Gaussian approximation can be viewed as a simplified version of the Herman–Kluk approximation in which the semiclassical prefactor is held fixed at its short-time limit of one. These studies also clearly demonstrate the power of the initial value approach in applications to problems with too many degrees of freedom to be treated rigorously quantum mechanically.[8,9] (See also the mixed semiclassical–classical methods developed recently by Sun and Miller.[11])

Returning to the Ar_nI^- photodetachment simulations,[1] one of the more striking results obtained in this work was that the number of trajectories required to converge the semiclassical spectra was found to increase only linearly with the number of vibrational degrees of freedom in the clusters. This is surprising because the volume of phase space that is sampled in the semiclassical calculations increases exponentially with the number of degrees of freedom, and one would generally expect the number of trajectories required for convergence to also scale exponentially with system size, just as the number of basis functions (and/or grid points) scales in any exact quantum mechanical calculation. The purpose of this article is to demonstrate exponential system-size scaling of the CFGA, and to suggest a simple explanation for the linear system-size scaling that was observed in the previous Ar_nI^- photodetachment simulations.

The generic system-size scaling of the CFGA can be revealed by applying the method to the following *N*-dimensional generalization of the Henon–Heiles model:[3]

$$H(\mathbf{p},\mathbf{q})=\tfrac{1}{2}\mathbf{p}^2+V(\mathbf{q}), \tag{1}$$

where

$$V(\mathbf{q})=\frac{1}{2}\sum_{i=1}^{N} q_i^2+\lambda\sum_{i=1}^{N-1}(q_i^2 q_{i+1}-q_{i+1}^3/3), \tag{2}$$

with $\lambda=0.118\,03$. This Hamiltonian has been used to calculate Franck–Condon spectra for initial wave functions of the form

$$\psi_0(\mathbf{q})=\pi^{-N/4}e^{-(\mathbf{q}-\mathbf{q}')^2/2}, \tag{3}$$

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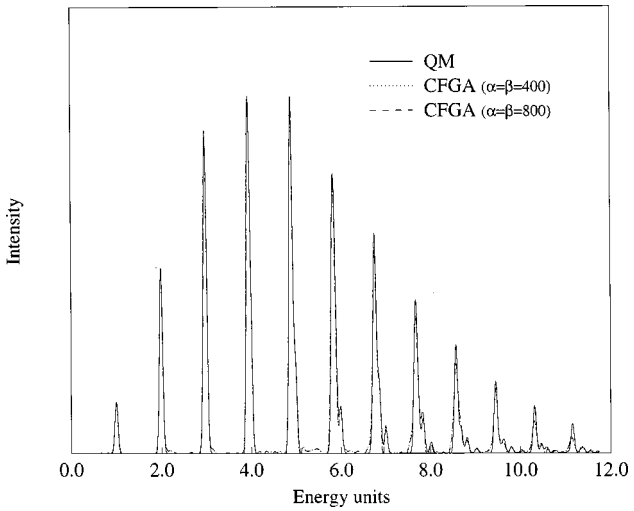

FIG. 1. Quantum mechanical (QM) and semiclassical (CFGA) Franck–Condon spectra for the model Henon–Heiles problem with $N=2$ degrees of freedom. The semiclassical results are shown for two sets of Filinov parameters ($\alpha=\beta=400$ and 800). Both of the semiclassical spectra are well converged with respect to the number of trajectories.

with a displacement of $q_i'=2$ for $i=1,2,...,N$, and the coordinates $\mathbf{q}$ can be taken to represent a set of normal vibrational modes.

The semiclassical calculations were performed in the same way as those described in Ref. 1. The initial phase space was sampled at random from the short-time limit of the CFGA integrand, and Hamilton's equations of motion, together with the classical action and monodromy matrix for each trajectory, were propagated using a fourth-order symplectic integrator. The Franck–Condon spectrum for the model problem with $N=2$ degrees of freedom has also been calculated quantum mechanically for comparison using the symmetric split operator method of Feit and Fleck.[12] Finally, each computed spectrum has been convoluted using a Gaussian window function with full width at half-maximum of 0.1 energy units.

The resulting semiclassical and quantum mechanical $N=2$ Franck–Condon spectra are shown in Fig. 1. The level of agreement between quantum mechanical and semiclassical results is excellent, as shown in the first CFGA studies of this problem by Walton and Manolopoulos.[3] The two sets of semiclassical results shown in Fig. 1 have been obtained using Filinov parameters $\alpha=\beta=400$ and $\alpha=\beta=800$, both of which are well converged with respect to the number of trajectories.[13] Given the good agreement between the two sets of semiclassical results, the Filinov parameters $\alpha=\beta=400$ have been selected to study further model problems with up to $N=10$ degrees of freedom. This will provide a fair comparison with the previous work,[1] in which the same parameters were used in all semiclassical calculations following a preliminary comparison with exact quantum results for the model photodetachment of the smallest cluster, Ar_2I^-.

The convergence of the CFGA spectra with respect to the number of trajectories for model problems with $N=2,4,...,10$ degrees of freedom is shown in Fig. 2. In conjunction with this figure, the number of trajectories required for convergence is plotted against N in Fig. 3(a). The number of trajectories required for convergence increases exponentially with the number of degrees of freedom in the model problems.

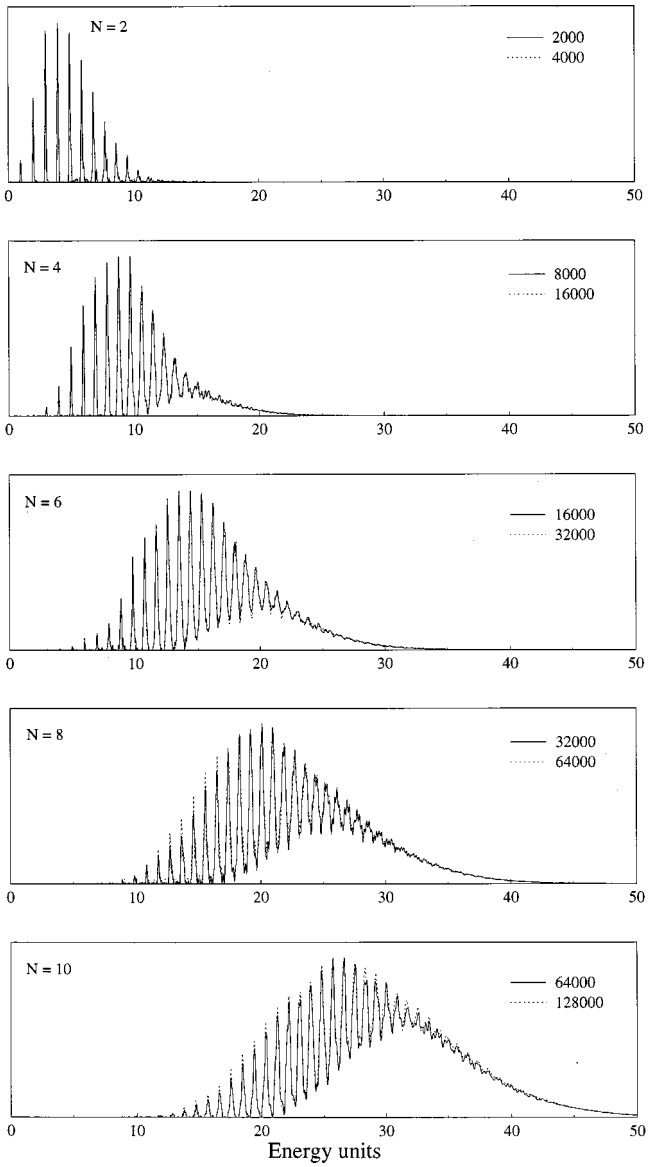

FIG. 2. Convergence of the CFGA with respect to the number of trajectories (using Filinov parameters $\alpha=\beta=400$) for the model Franck–Condon spectra with $N=2,4,...,10$ degrees of freedom.

It is reasonable to assume that any explanation for the contrasting system-size scaling observed in the Ar_nI^- photodetachment simulations and the generalized Henon–Heiles problems might lie in the qualitative differences between the associated spectra: recall that the Ar_nI^- photodetachment spectra are dominated by $\mathbf{0}\rightarrow\mathbf{0}$ vibrational transitions,[1] while many more final states can be seen to contribute to the present generalized Henon–Heiles Franck–Condon spectra. These differences can be quantified using the anharmonic normal mode (ANM) approximation[2] to calculate $\mathbf{0}\rightarrow\boldsymbol{\nu}_f$ Franck–Condon factors in order to obtain an estimate of the number of final quantum states $\boldsymbol{\nu}_f$ that make a significant contribution to the spectra in each of the two sets of systems.

As expected, in the Ar_nI^- clusters the $\mathbf{0}\rightarrow\mathbf{0}$ transition

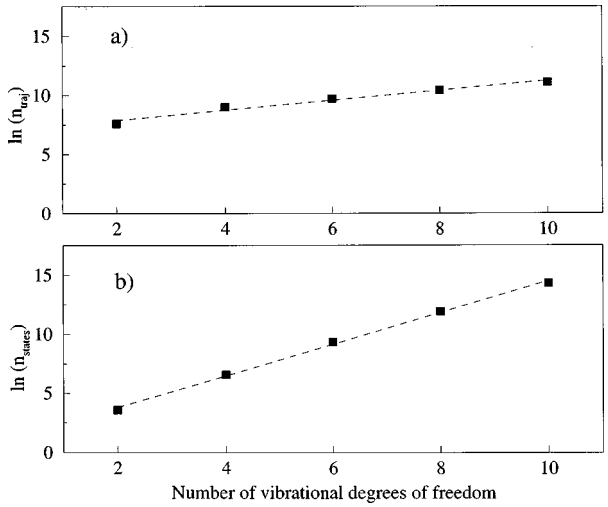

FIG. 3. (a) The number of trajectories (n_{traj}) required for convergence of the CFGA compared with the number of degrees of freedom in the model Henon–Heiles problems. (b) The number of final quantum states (n_{states}) required to account for 99% of the total transition probability (within the anharmonic normal mode approximation) compared with the number of degrees of freedom.

accounts for the majority (86% average) of the total transition probability to the two (X and I) neutral cluster surfaces, while the inclusion of the $\mathbf{0}\rightarrow\mathbf{1}$ transitions (i.e., 0,0,...,0 $\rightarrow$0,0,...,1, etc.) in these calculations accounts for virtually all (97% average) of the remaining probability. Therefore, to a first approximation, the number of final quantum states that contribute to the Ar_nI^- photodetachment spectra increases approximately linearly with the number of vibrational degrees of freedom, simply because the total number of possible $\mathbf{0}\rightarrow\mathbf{0}$ and $\mathbf{0}\rightarrow\mathbf{1}$ vibrational transitions increases linearly with increasing cluster size.

The present model problems exhibit very different behavior, and the number of quantum states that make a significant contribution to each of the $N=2,4,...,10$ Franck–Condon spectra are shown in Fig. 3(b). In these ANM calculations, a final quantum state $\boldsymbol{\nu}_f$ was deemed to contribute if it had an associated Franck–Condon factor that was greater than or equal to 1% of the maximum Franck–Condon factor in the particular model problem. It is clear from Fig. 3(b) that, like the number of trajectories required for convergence, the number of final quantum states that contribute to the Franck–Condon spectra in the model problems increases exponentially with the number of degrees of freedom.

On the basis of the above ANM results and the observed system-size scaling of the CFGA in each of the two systems, it appears that the effort required to implement the approximation is directly proportional to the number of quantum states that contribute to the Franck–Condon spectrum, even though the Monte Carlo algorithm always explores an initial phase space that grows exponentially with system size. The linear system-size scaling observed in the earlier Ar_nI^- photodetachment simulations now seems to be a consequence of the special properties of the clusters. The anion and neutral clusters have similar equilibrium geometries, so that the number of quantum states accessed following photodetachment increases only approximately linearly with the number of degrees of freedom. This is clearly not the case in the series of model problems considered here, where the number of final quantum states that contribute to the spectra increases exponentially with the number of degrees of freedom.

The linear system-size scaling observed in the Ar_nI^- photodetachment simulations is still encouraging, since it suggests that the number of trajectories required for convergence will increase linearly with increasing degrees of freedom for problems of linear complexity. However, as shown here, this number will increase exponentially with increasing degrees of freedom for problems of exponential complexity. It is worth noting that energy resolution will play an important part in determining this number since more trajectories are required to converge semiclassical calculations over long time scales. As indicated in the Ar_nI^- $(n=2-6)$ ANM calculations, it is sometimes possible to identify a contracted basis set which reflects the linear complexity of a problem and could allow a quantum calculation with a basis that scales more favorably than exponentially with increasing degrees of freedom. Nevertheless, the semiclassical initial value approach taken here would still compare favorably because the method appears to reflect problem complexity automatically, without the need to make an inspired choice of basis functions.

The author wishes to thank David Manolopoulos for many helpful discussions and also Jeremy Hulme for making some of his computer programs available.

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[13] In the limit as the Filinov parameters α and β tend to infinity, the CFGA reduces to the standard Herman–Kluk expression for the autocorrelation function of a Gaussian initial wave packet. However, this expression can be difficult to converge by Monte Carlo and it is more efficient to use the cellularized method with large (but finite) Filinov parameters, so as to allow one to converge the approximation without loss of accuracy.