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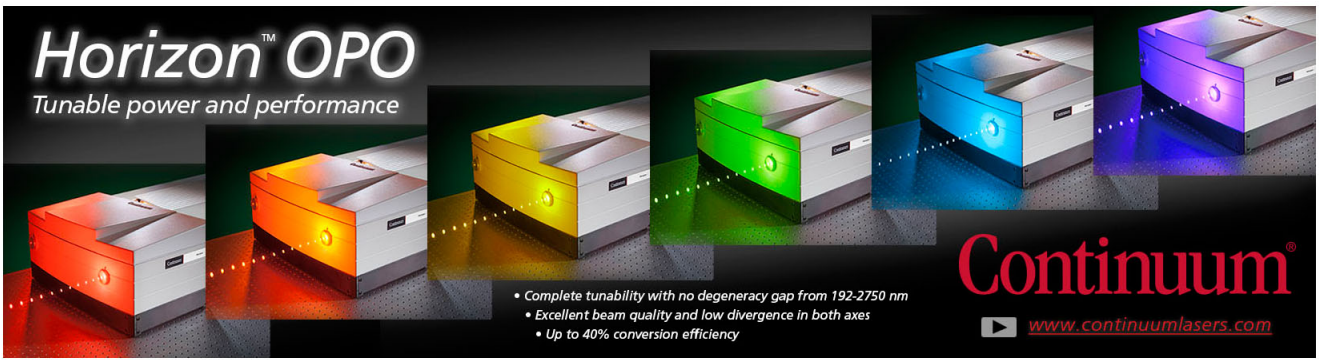

Simplified calculation of the stability matrix for semiclassical propagation

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We present a simple method of calculation of the stability (monodromy) matrix that enters the widely used semiclassical propagator of Herman and Kluk and almost all other semiclassical propagators. The method is based on the unitarity of classical propagation and does not involve any approximations. The number of auxiliary differential equations per trajectory scales linearly rather than quadratically with the system size. Just the first derivatives of the potential surface are needed. The method is illustrated on the collinear H_3 system. © *2000 American Institute of Physics.* [S0021-9606(00)01045-X]

I. INTRODUCTION

Recently the initial value representation (IVR) semiclassical propagation methods have been used for a variety of problems from the photodissociation[1] and reactive scattering[2–4] to complex molecular systems,[5–7] condensed phase problems,[8–12] and nonadiabatic dynamics.[13–16] Semiclassical propagators, with the propagator of Herman and Kluk (HK)[17–22] being the most widely used, are based on propagation of classical trajectories that have phases and amplitudes associated with them. This requires calculation of the stability (or monodromy) matrix $\mathbf{M}$, that shows the sensitivity of the final position and momentum of a trajectory to the initial conditions. This matrix is usually calculated by solving $4N^2$ additional differential equations for an N-dimensional system which require the second derivatives of the potential.

As applications of semiclassical propagation methods move towards large systems, the numerical effort of obtaining $\mathbf{M}$ becomes an issue. The quadratic scaling with N of the number of differential equations per trajectory is avoided in several recent works: through a decoupling approximation in Ref. 12, through the harmonic approximation to a potential in Ref. 23. The method of Ref. 11 avoids the calculation of the stability matrix by introducing a momentum discontinuity. A different semiclassical propagator,[24] based on the coherent state representation, also bypasses the stability analysis. An integral over a swarm of classical trajectories, derived from the unitary condition on the propagator, weighs each classical trajectory.

In this article we present a simple way to calculate the stability matrix with the *linear* rather than quadratic scaling with N of the number of auxiliary equations *without approximations*, that does not require the second derivatives of the potential. The method is described in Sec. II and it is illustrated on the collinear H_3 system using the IVR propagator of Herman and Kluk. It can be used in any semiclassical propagator that uses the trajectory stability analysis. Section III concludes the work.

II. CALCULATION OF THE STABILITY MATRIX USING UNITARITY OF CLASSICAL PROPAGATION

The HK propagator in N dimensions, generalized to include the width parameters as a matrix, is

$$K^{sc}(\mathbf{x}',t;\mathbf{x},0)=\frac{1}{(2\pi)^N}\int\int d\mathbf{p}_0\, d\mathbf{q}_0\, R_{pqt}e^{\imath S_{pqt}} \times g_\gamma(\mathbf{q}_t,\mathbf{p}_t,\mathbf{x}')g_\gamma^*(\mathbf{q}_0,\mathbf{p}_0,\mathbf{x}). \tag{1}$$

The function

$$g_\gamma(\mathbf{q}_t,\mathbf{p}_t,\mathbf{x})=\left(\frac{\det(\mathbf{\Gamma})}{\pi^N}\right)^{1/4} \times\exp(-\tfrac{1}{2}(\mathbf{x}-\mathbf{q}_t)\mathbf{\Gamma}(\mathbf{x}-\mathbf{q}_t)+\imath\mathbf{p}_t\cdot(\mathbf{x}-\mathbf{q}_t)), \tag{2}$$

is a complex Gaussian with the diagonal width matrix $\mathbf{\Gamma}=\{\gamma_i\}$. All γ_i are positive real parameters. Vectors $\mathbf{q}_0=(q_0^1,\ldots,q_0^N)$ and $\mathbf{p}_0=(p_0^1,\ldots,p_0^N)$ are initial conditions of a classical trajectory at time zero and vectors $\mathbf{q}_t=(q_t^1,\ldots,q_t^N)$ and $\mathbf{p}_t=(p_t^1,\ldots,p_t^N)$ are its coordinates and momenta at time t. S_{pqt} is the classical action,

$$S_{pqt}=\int_0^t[\mathbf{p}_{t'}\cdot\dot{\mathbf{q}}_{t'}-H(\mathbf{p}_{t'},\mathbf{q}_{t'},t')]dt'. \tag{3}$$

The prefactor involving the stability (or monodromy) matrix elements is

$$R_{pqt}=\sqrt{\det(\mathbf{B})}, \tag{4}$$

with the matrix elements $\mathbf{B}=\{b_{ij}\}$ being

$$b_{ij}=\frac{1}{2}\left(\sqrt{\frac{\gamma_i}{\gamma_j}}\frac{\partial p_t^i}{\partial p_0^j}+\sqrt{\frac{\gamma_j}{\gamma_i}}\frac{\partial q_t^i}{\partial q_0^j} -\imath\sqrt{\gamma_i\gamma_j}\frac{\partial q_t^i}{\partial p_0^j}+\frac{\imath}{\sqrt{\gamma_i\gamma_j}}\frac{\partial p_t^i}{\partial q_0^j}\right). \tag{5}$$

The square root in Eq. (4) is chosen to make R_{pqt} a continuous function of time.[20] The HK propagator is unitary, i.e., it preserves the normalization of the wave function, within the stationary phase approximation.[19] Most of the other semiclassical propagators are also based on the propagation of classical trajectories with contribution of each trajectory being a function of the stability matrix elements.

The stability matrix, $\mathbf{M}(t_2,t_1)$, of a trajectory $\{\mathbf{q}_t,\mathbf{p}_t\}$ evolving in time under the Hamiltonian H, is a function of initial and final times t_1 and t_2

$$\mathbf{M}(t_2,t_1)=\begin{pmatrix} \dfrac{\partial \mathbf{p}_{t_2}}{\partial \mathbf{p}_{t_1}} & \dfrac{\partial \mathbf{p}_{t_2}}{\partial \mathbf{q}_{t_1}} \\ \dfrac{\partial \mathbf{q}_{t_2}}{\partial \mathbf{p}_{t_1}} & \dfrac{\partial \mathbf{q}_{t_2}}{\partial \mathbf{q}_{t_1}} \end{pmatrix}. \tag{6}$$

The time evolution of $\mathbf{M}$ is described by a matrix equation of $2N\times 2N$ size,

$$\frac{d\mathbf{M}(t,t_1)}{dt}=\begin{pmatrix} 0 & \dfrac{\partial^2 H}{\partial \mathbf{q}^2} \\ \dfrac{\partial^2 H}{\partial \mathbf{p}^2} & 0 \end{pmatrix}\mathbf{M}(t,t_1), \tag{7}$$

where $\partial^2 H/\partial \mathbf{q}^2$ is the Hessian matrix. The initial condition of $\mathbf{M}$ is unitary, $\mathbf{M}(t_1,t_1)=\mathbf{1}$. Solution of Eq. (7) requires the second derivatives of the potential.

Alternatively, we use the unitarity property of the stability matrix, that can be verified by applying the chain rule of differentiation,

$$\mathbf{M}(t_3,t_1)=\mathbf{M}(t_3,t_2)\mathbf{M}(t_2,t_1), \tag{8}$$

to avoid the unfavorable quadratic scaling of Eq. (7) with the system size. Equation (8) allows one to restart the matrix $\mathbf{M}$ at some intermediate time t with the unitary initial condition. Extending this idea, we can use a unitary initial condition for $\mathbf{M}$ at every time step Δt and perform the partial differentiation numerically. At *each* time step, following a ''central'' trajectory

$$\mathbf{z}_0(t)=\{q_1(t),\ldots,q_N(t),p_1(t),\ldots,p_N(t)\} \tag{9}$$

contributing to the propagator, we will propagate $2N$ additional classical trajectories, whose initial conditions differ from $\mathbf{z}_0(t)$ by a displacement in one of the variables,

$$\begin{aligned} &\mathbf{z}_1(t)=\{q_1(t)+\Delta q_1,\ldots,q_N(t),p_1(t),\ldots,p_N(t)\},\\ &\qquad\cdots\\ &\mathbf{z}_N(t)=\{q_1(t),\ldots,q_N(t)+\Delta q_N,p_1(t),\ldots,p_N(t)\},\\ &\mathbf{z}_{N+1}(t)=\{q_1(t),\ldots,q_N(t),p_1(t)+\Delta p_1,\ldots,p_N(t)\},\\ &\qquad\cdots\\ &\mathbf{z}_{2N}(t)=\{q_1(t),\ldots,q_N(t),p_1(t),\ldots,p_N(t)+\Delta p_N\}. \end{aligned} \tag{10}$$

Then, the elements m_{ij} of $\mathbf{M}$ are

$$m_{ij}=\frac{\partial z^i(t+\Delta t)}{\partial z^j(t)}=\frac{z_j^i(t+\Delta t)-z_0^i(t+\Delta t)}{\Delta z_j}, \tag{11}$$

with z_j^i designating the ith component of the jth trajectory. The elements for any initial time t_1 and final time t_2 can thus be found as a product

$$\begin{aligned} \mathbf{M}(t_2,t_1)=&\mathbf{M}(t_2,t_2-\Delta t)\cdot\mathbf{M}(t_2-\Delta t,t_2-2\Delta t)\\ &\cdot\ldots\cdot\mathbf{M}(t_1+\Delta t,t_1), \end{aligned} \tag{12}$$

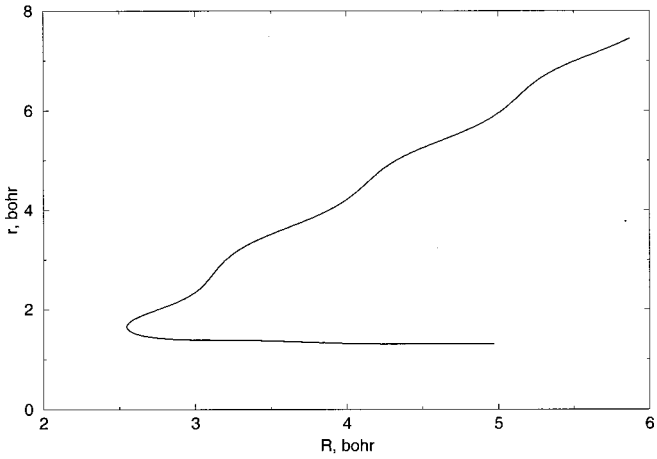

FIG. 1. A reactive trajectory for the collinear H_3 system in Jacobi coordinates.

where the number of terms is $(t_2-t_1)/\Delta t$. A more accurate central difference scheme for m_{ij} requires $4N$ trajectories with displacements $\pm\Delta q_i,\pm\Delta p_i$. This was used in the example below. The number of equations per trajectory will *scale linearly* with N, as $4N$ for the central difference scheme of numerical differentiation above, and the *second derivatives of the potential are not required*. Matrix multiplication gives overall N^3 scaling to both, the present method of Eqs. (10) and (12) and to the standard method of Eq. (7). However, the main computational effort goes into solving of the differential equations and this is why the present method might be advantageous.

The multiplication time step Δt of Eq. (12) can be the same as the trajectory propagation time step dt or larger, as long as the numerical differentiation remains accurate. The accuracy of $\mathbf{M}$ can be monitored by the deviation of the determinant of $\mathbf{M}$ from 1. Since the multiplication of small matrices is a minor numerical effort compared to the trajectory propagation, and since smaller Δt gives more accurate numerical derivatives, we take the trajectory propagation time step dt to be equal to Δt below.

As an example we will look at the amplitude $|R_{pqt}|$ in the HK propagator, which is a function of the stability matrix elements, of a single reactive trajectory on the potential surface for the collinear H_3 system. Figure 1 shows a typical reactive trajectory with initial conditions $\mathbf{z}_0(0)=\{5.0,1.4,-7.0,0.0\}$ and which is the center of a Gaussian with $\mathbf{\Gamma}=\{12.0,18.7\}$. Other details of the calculation are the same as in Ref. 2. The propagation time step dt is the same for the central and auxiliary trajectories and equal to Δt.

R_{pqt} of the trajectory is given by Eq. (4). R_{pqt} found with Eq. (7) and with Eqs. (10) and (12) are shown in Fig. 2. The two curves agree within 5×10^{-4}. The propagation required about 3000 time steps, $\Delta t=0.574$ a.u. Figure 3 shows the convergence of $|R_{pqt}|$ with respect to the time step for the present method. The accuracy of the determinant, $|\det(\mathbf{M})-1|$, was better than 10^{-8} at all times. Figure 4 shows the accuracy of $|R_{pqt}|$ for several initial displacements in Eq. (10). We obtained stable results for displacements $10^{-4}-10^{-6}$ (the same in all coordinates). Equation (12)

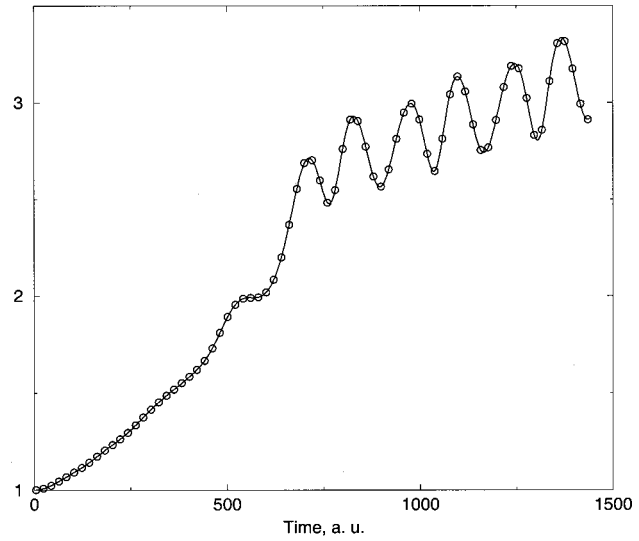

FIG. 2. The amplitude $|R_{pqt}|$ of a trajectory in HK propagator found from the matrix Eq. (7), shown with the solid line, and as a product from Eqs. (10) and (12), shown with circles. Time step is $\Delta t = 0.574$ a.u.

might be numerically inaccurate for long-time propagation of chaotic trajectories requiring a very large number of steps.

III. SUMMARY

As initial value representation semiclassical propagation methods become widely used for large systems—complex molecules and condensed phase systems, the computational effort going into the calculation of the stability (monodromy) matrix **M** becomes a concern. The typical way of finding **M** requires a solution of $4N^2$ auxiliary differential equations and the second derivatives of the potential for an N-dimensional system. We presented a simple way of calculating the stability matrix for classical trajectories based on its unitarity. The number of differential equations per trajectory scales linearly, as $4N$ for the central difference scheme.

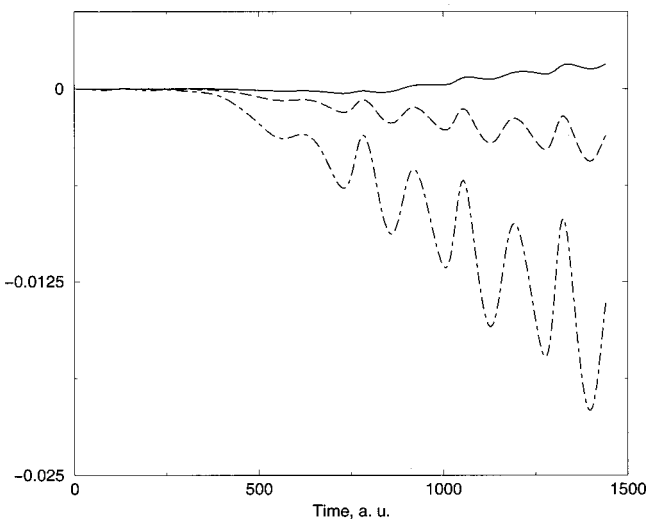

FIG. 3. Difference of the amplitude $|R_{pqt}|$ for $\Delta t = 0.574$ a.u. with amplitudes for $2\Delta t$ (solid line), $4\Delta t$ (dashed line), and $8\Delta t$ (dot-dashed line).

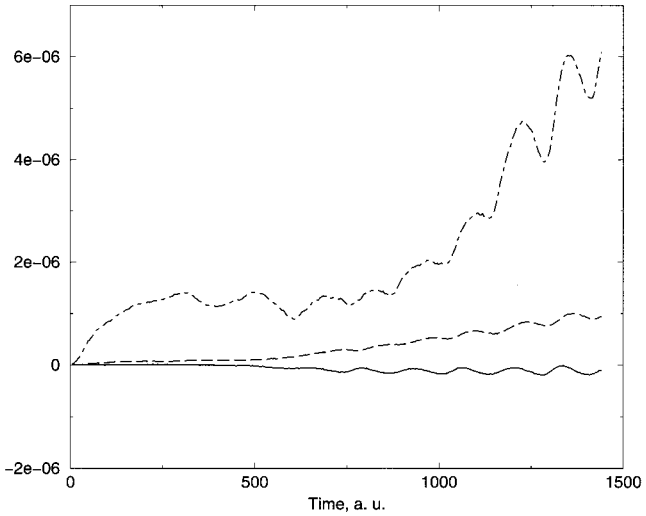

FIG. 4. Difference of the amplitude $|R_{pqt}|$ for initial displacement 10^{-5} with amplitudes for displacements 10^{-4} (solid line), 10^{-6} (dashed line), and 10^{-7} (dot-dashed line).

Only the first derivatives of the potential, that are often found along with the construction of the potential surface, are needed. The method does not involve any approximations. We illustrated it on the collinear H_3 system using IVR semiclassical propagator of Herman and Kluk and showed that it gives accurate amplitude R_{pqt} for a range of initial displacements and converges with respect to the time step. Our method may not be well-suited for chaotic systems that will require many thousands of time steps, something that was not tested in this work. However, we expect this way of finding the stability matrix to be useful for dynamics of large systems where its features will be an advantage.

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