A quasiclassical method which enables evaluation of complex autocorrelation function from classical trajectory calculations is proposed. The method is applied for two highly excited nonlinearly coupled harmonic oscillators in regimes prevailed either by regular or chaotic classical motions. A good agreement of classical and quantum autocorrelation functions is found within short (Ehrenfest) time limit. Fourier transforms of the autocorrelation functions provide moderate resolved energy spectra, where classical and quantum results nearly coincide. The actual energy levels are obtained from approximate short-time autocorrelation functions with the help of filter diagonalization. This study is a follow up to our previous work [P. Zdánska and N. Moiseyev, J. Chem. Phys. 115, 10608 (2001)], where the complex autocorrelation has been obtained up to overall phase factors of recurrences. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787489]
the required autocorrelation function at periodic time intervals. This designed coincidence enables us to obtain the relative phase between recurrences, and thus the complete autocorrelation function can be calculated: phase and amplitude.

We demonstrate our techniques for the model Pullen-Edmonds Hamiltonian of two nonlinearly coupled harmonic oscillators\cite{24,25} in Secs. V and VI. Our calculations give an evidence that the presented method works in regular and chaotic regimes alike, yet the calculations differ in the effort required. While in the regular case (Sec. V) a single periodic orbit is sufficient to follow the periodic motion, in the chaotic regime one has to define multiple periodic orbits to follow individual recurrences (Sec. VI).

The main importance of obtaining the autocorrelation function is that it can be used to obtain the energy spectrum, therefore in Sec. VII we demonstrate the application of Fourier transform and filter-diagonalization\cite{26,27} methods to calculate the energy spectra from classical approximations to autocorrelation functions. In Sec. VIII we present our conclusions.

II. WIGNER PHASE-SPACE APPROACH

The WPS method is a quasiclassical approach to quantum dynamical problems, consisting of three steps: (i) The initial phase-space density $P$ is obtained as a Wigner transform of the initial wave function $\Psi$,

$$P(q,p) = \frac{1}{(2\pi\hbar)^F} \int d\Delta q e^{ih\Delta p \cdot \Delta q} \times \Psi(q-\Delta q/2)\Psi^*(q+\Delta q/2),$$

where $F$ is the system dimension. $P$ is represented as the ensemble of phase-space points, $\{q_i,p_i\}$. Phase-space points are preferentially distributed in the region of $P$ such that the weight, $w_i=\int P(q,p)$, is ascribed to every randomly generated point $\{q_i,p_i\}$; the weight is compared with a randomly generated number, $\Omega<\max(P)$, and the point is selected if $w_i>\Omega$. (ii) Phase-space points, $\{q_i,p_i\}$, are evolved in time by classical propagation. The obtained trajectories, $\{q_i(t),p_i(t)\}$, represent the time-dependent classical phase-space density $P(t)$. (iii) The quantum expectation values, $\langle \hat{A} \rangle(t)$, defined as

$$\langle \hat{A} \rangle(t) = \langle \Psi|e^{-i\hat{H}t}|\hat{A}|e^{i\hat{H}t}\Psi \rangle$$

are approximated by the phase space integrals,

$$\langle \hat{A} \rangle(t) \approx \int dq \ dp \ A(q,p)P(q,p;t),$$

where $A$ corresponds with $\hat{A}$ through the Wigner-Weyl transform of the operator $\hat{A}$ given by

$$A(q,p) = \int d\Delta q e^{ih\Delta p \cdot \Delta q} \Delta q |\hat{A}|q+\Delta q/2$$

$$= \int d\Delta p e^{ih\Delta q \cdot \Delta p} \Delta p |\hat{A}|p+\Delta p/2.$$  

In practice, $\langle \hat{A} \rangle(t)$ is evaluated by Monte Carlo integration over classical trajectories,

$$\langle \hat{A} \rangle(t) \approx \sum_i A[q_i(t),p_i(t)].$$

Following this, the survival probability $|C(t)|^2$ defined as the absolute value squared of the autocorrelation function $C(t)$,

$$C(t) = \langle \Psi|e^{-i\hat{H}t}|\Psi \rangle,$$

is obtained for $\hat{A}$ being the initial density operator, $|\Psi\rangle\langle\Psi|$; the survival probability is approximated within the WPS method by

$$|C(t)|^2 \approx \sum_i P[q_i(t),p_i(t)].$$

III. PHASE OF AUTOCORRELATION FUNCTION

Calculation of the complex autocorrelation function is considered fully within the realm of the WPS method, namely, the phase is calculated using expectation values, which are approximated by Eqs. (3) and (6). Let the phase, $\phi_C(t)$, of the autocorrelation function be defined as

$$C(t) = |C(t)|e^{i\phi_C(t)}.$$  

By differentiating the identity $C(t)/C^*(t) = \exp[2i\phi_C(t)]$ we obtain the expression for the time derivative of the phase given by

$$\frac{d\phi_C}{dt} = -\hbar^{-1}\Re(\hat{H})\Psi,$$

where

$$\langle \hat{H} \rangle = \frac{\langle \Psi|e^{i\hat{H}t}\hat{P}|e^{-i\hat{H}t}\Psi \rangle}{\langle C \rangle^2},$$

and $\hat{P}$ is the density operator defined as

$$\hat{P} = |\Psi\rangle\langle\Psi|.$$  

Equation (11) allows us to calculate the phase using the time-dependent expectation values, which in turn are accessible by the WPS approach using Eqs. (3) and (6). The survival probability, $|C|^2$, is obtained using the known WPS approximation given by Eq. (8). The nominator is defined as the expectation value $\langle \hat{P} \hat{H} \rangle(t)$ of the product operator $\hat{A}_H = \hat{P} \hat{H}$.

Following the WPS approach, we calculate the Wigner-Weyl transform $A_H$ of the operator $\hat{A}_H$ using Eqs. (4) and (5). It is convenient to calculate separately the potential and kinetic contributions, $A_H = A_v + A_T$, where $A_v$ is the Wigner-Weyl transform of $A_v = \hat{P} \hat{V}$ and $A_T$ is the Wigner-Weyl transform of $\hat{A}_T = \hat{P} \hat{T}$. $A_v$ is calculated using Eq. (4) as long as $\hat{A}_v$ includes the potential operator commuting with coordinate representation,

$$A_v = \int d\Delta q e^{ih\Delta p \cdot \Delta q} \Delta q \Psi(q-\Delta q/2)\Psi^*(q+\Delta q/2) \times V(q+\Delta q/2).$$

The potential operator is expanded in Taylor series such that,
\[ V(q + \Delta q/2) = \sum_{n=0}^{\infty} \frac{\Delta q^n}{2^n n!} d^n V \Delta q^n. \]  

This result is substituted to Eq. (13). We use the following property of Fourier transform,

\[ \int d\Delta q e^{i\hbar p \cdot \Delta q} \Delta q \Psi(q - \Delta q/2) \Psi^*(q + \Delta q/2) \Delta q^n = (-i \hbar)^n \frac{\partial^n P}{\partial p^n}. \]  

and we obtain the series for \( A_v \) given by,

\[ A_v = \sum_{n=0}^{\infty} \frac{(-i \hbar)^n}{2^n n!} d^n V \frac{\partial^n P}{\partial q^n}. \]  

The Wigner-Weyl transform of \( \hat{A}_T \) is obtained in the same manner using the momentum representation, Eq. (5),

\[ A_T = \sum_{n=0}^{\infty} \frac{(-i \hbar)^n}{2^n n!} d^n T \frac{\partial^n P}{\partial p^n}. \]  

The Wigner-Weyl transform \( A_H \) of \( \hat{A}_H \) is a complex function given by the series for its real and imaginary parts,

\[ \Re A_H = \sum_{n=0}^{\infty} \left( \frac{-\hbar^2}{4} \right)^n \frac{1}{(2n)!} \int \frac{d^{2n} V \frac{\partial^{2n} P}{\partial q^{2n}}}{d^{2n} P \frac{\partial^{2n} q}{\partial p^{2n}}} + \frac{d^{2n} T \frac{\partial^{2n} P}{\partial q^{2n}}}{d^{2n} T \frac{\partial^{2n} q}{\partial p^{2n}}}, \]  

\[ \Im A_H = -\frac{i}{2} \sum_{n=0}^{\infty} \left( \frac{-\hbar^2}{4} \right)^n \frac{1}{(2n+1)!} \int \frac{d^{2n+1} V \frac{\partial^{2n+1} P}{\partial q^{2n+1}}}{d^{2n+1} P \frac{\partial^{2n+1} q}{\partial p^{2n+1}}} + \frac{d^{2n+1} T \frac{\partial^{2n+1} P}{\partial q^{2n+1}}}{d^{2n+1} T \frac{\partial^{2n+1} q}{\partial p^{2n+1}}} \]  

We obtain the WPS approximation for \( \langle \hat{H} \rangle_\Psi \) by substitutions into Eq. (11)—using Eqs. (6), (18), and (19) we obtain the WPS approximation of the nominator, while Eq. (8) is used for the denominator,

\[ \langle \hat{H} \rangle_\Psi = \frac{\Re A_H[q(t), p(t)]}{\Sigma_i \mathcal{P}[q(t), p(t)]}. \]  

The phase of the autocorrelation function is calculated using Eq. (10) such that,

\[ \frac{\partial \phi_c}{\partial t} = -\frac{i}{\hbar} \frac{\Re A_H[q(t), p(t)]}{\Sigma_i \mathcal{P}[q(t), p(t)]}. \]  

The phase of the autocorrelation function is calculated by numerical integration using the phase derivative over time. In cases where the autocorrelation function consists of well separated recurrences (see, e.g., Fig. 2), the phase derivative between the recurrences cannot be calculated for the reason of numerical inaccuracy. Therefore in such cases, the phase is known for individual recurrences only up to a constant phase factor. The solution of this difficulty is addressed in Sec. IV, where we define and evaluate a cross-correlation function, which coincides with the autocorrelation function at a single point within each recurrence.

A. Inconsistency within WPS approach: The harmonic approximation

In this section we discuss inconsistent expressions for autocorrelation function, which are derived using different algebraical approaches. Let us demonstrate this point for the case of autocorrelation amplitude, \( |C|^2 \). The derivation of the phase derivative, Eq. (10), is applicable also in the case of autocorrelation amplitude; we obtain

\[ \frac{\partial \ln |C|}{\partial t} = \frac{\Sigma_i \mathcal{A}_H[q(t), p(t)]}{\Sigma_i \mathcal{P}[q(t), p(t)]}. \]  

Another way to obtain the time derivative of the autocorrelation amplitude, is by differentiating Eq. (8); doing this and using Hamilton’s equations of motion we obtain the expression,

\[ \frac{\partial \ln |C|}{\partial t} = \frac{1}{2} \frac{\Sigma_i A[q(t), p(t)]}{\Sigma_i \mathcal{P}[q(t), p(t)]}, \]  

where

\[ A = \frac{dV}{dq} \frac{\partial P}{\partial p} + \frac{dT}{dp} \frac{\partial P}{\partial p}. \]  

By comparison of Eqs. (22) and (23) one can see that Eq. (23) is obtained from Eq. (22), when only the first term of the series for \( \mathcal{A}_H \) [in Eq. (19)] is included.

Similar discussion is possible for the time derivative of the autocorrelation phase. An alternative to the WPS approximation, Eq. (21), is the expression given by,

\[ \frac{\partial \phi_c}{\partial t} = \frac{\Sigma_i H[q(t), p(t)] P[q(t), p(t)]}{\Sigma_i \mathcal{P}[q(t), p(t)]}. \]  

[The proof of Eq. (25) can be found in Ref. 23.] Again, by comparison of Eqs. (21) and (25) one can see that Eq. (25) is obtained from Eq. (21), when only the first term of the series for \( \mathcal{A}_H \), Eq. (19), is included.

The existence of different formulas for same quantities, all consistent with the WPS assumption [Eq. (6)], represents the inherent error of the WPS approximation. One can see that Eq. (23) is obtained from Eq. (22) using the quadratic approximation, therefore the WPS approximation to autocorrelation amplitude is exact in the case of harmonic oscillator. On the other hand, Eq. (25) is given by the linear approximation to Eq. (21). As a consequence, using of Eq. (25) results in values of \( \partial \phi_c/\partial t \) which are incorrect for harmonic oscillator.

In order to clarify the role of the quadratic term in calculation of the phase derivative, let us consider the case of a coherent Gaussian wave packet given by,

\[ \Psi = \frac{1}{(\hbar \pi)^{3/4}} \exp \left( -\frac{|q - q_0|^2}{2\hbar} + \frac{i}{\hbar} q p_0 \right), \]  

where the harmonic Hamiltonian is given by, \( H = p^2/2 + q^2/2 \). Using Eq. (1) we obtain the corresponding Wigner distribution given by,
\[ \mathcal{P} = \frac{1}{(\hbar \pi)^d} \exp \left[ -\frac{(q-q_0)^2}{\hbar} - \frac{(p-p_0)^2}{\hbar} \right]. \]  

(27)

The Hamiltonian \( H \) and the Wigner distribution \( \mathcal{P} \) are substituted into Eq. (18). \( \mathcal{R}A_H \) can be written as the sum of zero-order and second-order terms, \( \mathcal{R}A_H = \mathcal{P}H + \mathcal{P}H^{(2)} \), where \( H^{(2)} \) is given by

\[ H^{(2)} = \frac{F\hbar}{2} \left[ \frac{1}{2}(p-p_0)^2 + (q-q_0)^2 \right]. \]  

(28)

The contribution of the zero-order term to \( \partial \phi_c / \partial t \), as defined by Eq. (25), is given by

\[ \frac{\partial \phi_c}{\partial t} \bigg|_{H} = \frac{F\hbar}{4} + \frac{q_0 + p_0}{2}. \]  

(29)

The contribution of the second term is calculated using the equation,

\[ \frac{\partial \phi_c}{\partial t} \bigg|_{H^{(2)}} = \frac{\Sigma H^{(2)}(q_c(t), p_c(t))}{\Sigma [\mathcal{P}(q_c(t), p_c(t))]}, \]  

(30)

and is given by

\[ \frac{\partial \phi_c}{\partial t} \bigg|_{H^{(2)}} = \frac{F\hbar}{4}. \]  

(31)

The sum of the zero- and second-order contributions leads to the correct result,

\[ \frac{\partial \phi_c}{\partial t} = \frac{F\hbar}{2} + \frac{q_0 + p_0}{2}, \]  

(32)

which is in agreement with the quantum-mechanical definition given by Eqs. (10) and (11). It is evident from this discussion that the second-order term is responsible for one half of the zero-point energy shift in the case of coherent harmonic motion. It is thus expected that an error of about one half of the zero-point energy is caused by omitting the quadratic term in series Eq. (18).

**IV. CROSS-CORRELATION FUNCTION**

In this section we show how over-all phase factors of autocorrelation recurrences can be obtained. Let us consider a quasiperiodic motion with the approximate period \( T \). Then we may assume that a recurrence in autocorrelation function occurs for time \( t = T \). The idea is to define the new function \( \Phi(t) \) such that \( \Phi(t = NT) = \Psi \) and therefore, after \( T, 2T, \ldots \) etc. periods the values of \( C(t = NT) \) are equal to \( X(t = NT) \),

\[ C(NT) = X(NT), \quad N = 0, 1, \ldots, \]  

(33)

where \( X(t) \) is defined as

\[ X(t) = \langle \Phi(t) | e^{-i\hbar \hat{H}/\hbar} | \Psi \rangle. \]  

(34)

The idea is to define \( \Phi(t) \) in such a way that there are no revivals in \( X(t) \) and therefore unlike \( C(t) \), \( X(t) \) does not drop to zero between the recurrences. In this way we avoid numerical difficulties in extracting time-dependent phase derivatives between recurrences where \( C(t) \sim 0 \). To assure this condition, it is reasonable to define \( \Phi(t) \) as the frozen wave packet moving according to the classical periodic contour. \( X(t) \) represents a cross-correlation function, however, notice that in this case the left vector \( \Phi(t) \) depends on \( t \) parametrically, in contrast to the most common definition of cross-correlation function.

**A. Classical periodic contour**

We define an approximate classical periodic contour (orbit), \([q_c(t), p_c(t)] \), such that \([q_c(0), p_c(0)] = [q_c(T), p_c(T)] \). Except for approximately following the motion of the classical phase-space density, the periodic contour can be arbitrary; here we suggest the following procedure:

(i) positions and momenta of evolving trajectories are weighted by \( \mathcal{P}(q_c(T), p_c(T)) \), to give a large preference to those contributing to a given autocorrelation recurrence. Further we confine to trajectories falling within a small energy interval \( E_0 - \Delta E \leq \hat{H}[q_c(t), p_c(t)] \leq E_0 + \Delta E \); this is especially reasonable in cases when the wave function bifurcates due to time evolution. The first estimate of the classical contour according to this procedure is given by

\[ q_{c,0}(t) = \frac{\Sigma q_c(t) \mathcal{P}(q_c(T), p_c(T)) \Delta_i}{\Sigma \mathcal{P}(q_c(T), p_c(T)) \Delta_i}, \]  

\[ p_{c,0}(t) = \frac{\Sigma p_c(t) \mathcal{P}(q_c(T), p_c(T)) \Delta_i}{\Sigma \mathcal{P}(q_c(T), p_c(T)) \Delta_i}, \]  

(35)

where \( \Delta_i = 1 \) for \( E_0 - \Delta E \leq \hat{H}[q_c(t), p_c(t)] \leq E_0 + \Delta E \) and \( \Delta_i = 0 \) otherwise. \([q_{c,0}(t), p_{c,0}(t)] \) satisfy the condition of approximately following the classical phase-space packet.

(ii) The second condition is that the contour must form a closed loop, which is accomplished by using the back-and-forth Fourier transform:

\[ q_c(t) = \sum_n \exp \left( -i \frac{2\pi nt}{T} \right) \times \left[ \int_{0}^{T} dt' \exp \left( i \frac{2\pi nt'}{T} \right) q_{c,0}(t') \right], \]  

(36)

where \( n \) acquires small integer values \( p_c(t) \) is obtained similarly.

**B. Frozen wave packet**

We define a wave function \( \Phi(t) \) given by

\[ \Phi(t) = e^{i\hat{H}t} [p_c(t) - p_c(0)] q_{c,0} - e^{-i\hat{H}t} [q_c(t) - q_c(0)] \Psi, \]  

(37)

that represents a frozen wave packet which keeps the shape of the initial wave function \( \Psi \) while its position is changed according to the classical periodic contour, \([q_c(t), p_c(t)] \). The wave packet \( \Phi(t) \) acquires the important property, \( \Phi(NT) = \Psi \). \( \Phi(t) \) is given by

\[ \Phi(t) = \frac{1}{(\hbar \pi)^{d/4}} \exp \left[ -\frac{|q - q_c(0) - q_c(t)|^2}{2\hbar} \right. \]

\[ + \frac{i}{\hbar} q \left[ p_c(0) + p_c(t) + \frac{i}{\hbar} p_0 \cdot [q_c(0) - q_c(t)] \right], \]  

(38)
for the case of initial Gaussian wave packet defined by Eq. (26).

C. Absolute value and phase of cross-correlation function

Calculation of complex cross-correlation function \( X(t) \) by the WPS approach is similar as in the case of the autocorrelation function. The absolute value square \( |X|^2 \) is obtained as the expectation value of the density operator,

\[
\hat{\rho}_f(\tau) = \hat{\Phi}(\tau) \hat{\Phi}^*(\tau),
\]

such that

\[
|X|^2 \approx \sum_i \rho_i(\tau) \rho_i(\tau). \tag{40}
\]

where

\[
\rho_i(\tau) = \int d\Delta \rho e^{i\hbar \Delta \phi} (\rho) \Delta \rho \rho(\Delta \rho/2; t) = \Delta \rho \rho^*(\Delta \rho/2; t). \tag{41}
\]

The phase, \( \phi_X \), of the cross-correlation function is defined as

\[
X(t) = |X(t)| e^{i\phi_X(t)}. \tag{42}
\]

By differentiating the identity \( X(t)/X^*(t) = \exp[2i\hbar t] \), we derive the expression for the time derivative of \( \phi_X \) given by

\[
\frac{d\phi_X}{dt} = \frac{1}{\hbar} \{ -\hat{\rho}_f, \hat{\rho}_f \} + \hat{\rho}_f \{ \hat{\rho}_f, \hat{\rho}_f \}, \tag{43}
\]

where the notation \( \left\langle \hat{\rho}_f \right\rangle_\hat{\phi} \), \( \hat{\phi} \), stands for

\[
\left\langle \hat{\rho}_f \right\rangle_\hat{\phi} = \frac{\langle \Psi e^{i\hbar \hat{\phi}} \hat{\rho}_f | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{44}
\]

The WPS approximation to \( \langle \hat{\rho}_f \rangle_\hat{\phi} \) is obtained as follows: the nominator, \( \hat{\rho}_f \hat{\phi}_f \), is evaluated using Eq. (6), where \( \hat{\phi}_f = \hat{\phi} \hat{\rho}_f \); and the denominator, \( |X|^2 \), is evaluated using Eq. (40).

\[
\langle \hat{\rho}_f \rangle_\hat{\phi} \approx \frac{\sum_i A_{i\phi} \Psi_i(\tau) \Psi_i(\tau)}{\sum_i \rho_i(\tau) \rho_i(\tau)}. \tag{45}
\]

The Wigner-Weyl transforms, \( A_{i\phi}, A_{i\phi}, A_{i\phi} \), are complex functions whose only real parts are used to calculate the cross-correlation phase [Eq. (43)]. These are listed below:

\[
\begin{align*}
\Re A_{i\phi} &= \Re A_{i\phi} H + \sum_{n = 1}^{\infty} \left( \frac{\hbar^2}{4} \frac{1}{(2n)!} \right) \\
\times & \left( \frac{\partial^2 V}{\partial q^n} \frac{\partial^2 p_\phi}{\partial p^{2n}} + \frac{\partial^2 T}{\partial q^n} \frac{\partial^2 p_\phi}{\partial p^{2n}} \right), \\
\Re A_{i\phi} &= \Re A_{i\phi} q_\phi, \tag{46}
\end{align*}
\]

\[
\Re A_{i\phi} = \Re A_{i\phi} p_\phi.
\]

The WPS approximations for the integrals \( \Re(\hat{H}) \phi, \Re(\hat{q}) \phi, \Re(\hat{p}) \phi \), are given by

\[
\begin{align*}
\Re(\hat{H}) \phi &= \frac{\sum_i \Re A_{i\phi} \Psi_i(\tau) \Psi_i(\tau)}{\sum_i \rho_i(\tau) \rho_i(\tau)}, \\
\Re(\hat{q}) \phi &= \frac{\sum_i \Re A_{i\phi} \Psi_i(\tau) \Psi_i(\tau)}{\sum_i \rho_i(\tau) \rho_i(\tau)}, \\
\Re(\hat{p}) \phi &= \frac{\sum_i \Re A_{i\phi} \Psi_i(\tau) \Psi_i(\tau)}{\sum_i \rho_i(\tau) \rho_i(\tau)}. \tag{47}
\end{align*}
\]

To summarize, the complex cross-correlation function \( X(t) \) is calculated using the WPS approach. The absolute value \( |X| \) is obtained using Eq. (40), while the phase \( \phi_X \) is obtained by numerical integration of its time derivative, \( \partial \phi_X / \partial t \), which is given by Eqs. (43) and (47). The cross-correlation function \( X(t) \) can be evaluated numerically in the time interval from \( t = 0 \) to \( t = NT \), as long as it does not include revivals nor drops to zero. As discussed before, this is not true for the autocorrelation function \( C(t) \) which can be evaluated from classical trajectory calculations for individual recurrences only up to the overall phase factors. Using the equivalence Eq. (33), we obtain the correct phase of the autocorrelation function at \( T, 2T, \ldots \) from the calculated complex cross-correlation function. Thus the missing overall phases of autocorrelation recurrences are determined and the classical complex autocorrelation function is obtained.

V. ILLUSTRATION FOR REGULAR SYSTEM

The Pullen-Edmonds Hamiltonian is given by

\[
V = q_1^2/2 + q_2^2/2 + \lambda q_1^2 q_2^2, \tag{48}
\]

\[
T = p_1^2/2 + p_2^2/2.
\]

It represents two nonlinearly coupled harmonic oscillators. For energies beyond a given energy limit \( E_1 \), the system becomes mixed regular and chaotic. For the \( \lambda \) chosen, \( \lambda = 0.05 \), the energy limit \( E_1 \approx 1 \) a.u. The initial wave packet \( \Psi \) is given by the Gaussian function, Eq. (26). The initial position of \( \Psi \) in the phase space is \( q_0 = 4 \) a.u., \( 2.957 \) a.u., \( p_0 = [0,0] \). The corresponding energy expectation value is 21 a.u., which is set far in classical mixed regular-chaotic regime. The prevailer motion for this wave packet is regular, as shown in Ref. 23. The system is illustrated in Fig. 1. The contour plot of potential illustrates its nonlinearity which displays itself by deviation from circular curvature. The wave packet, which is evolved, approximately, for one classical period, deforms and starts to develop nodes, but stays localized.

We confine our study to a short-time propagation, for three classical periods. This is approximately the Ehrenfest time for the studied system, where all trajectories acquire the same Maslov indices at a time, as shown in Ref. 23. Once this condition is satisfied, the WPS approximation given by Eq. (6) is correct. The quantum-mechanical propagation, which serves as the benchmark for our study, allows us to calculate the exact autocorrelation function [Eq. (7)] for this time period. The autocorrelation function \( C(t) \) includes three well distinguished recurrences, as shown in Fig. 2.
FIG. 1. One-period wave packet evolution. The Pullen-Edmonds potential is drawn by dashed contours. The wave packet is shown at times \( t_1 = 0 \), \( t_2 = 2.3 \text{ a.u.} \), \( t_3 = 3.5 \text{ a.u.} \), and \( t_4 = 4.65 \text{ a.u.} \). The evolved wave packet intersects the closed contour \([\text{Eqs. (35)–(36)}]\), which serves in the definition of the cross-correlation function.

The classical trajectory simulation is performed for an ensemble of trajectories, \( [q_c(t), p_c(t)] \), which are chosen by means of preferential sampling of the initial phase-space density, \( \mathcal{P} \). \( \mathcal{P} \) is defined by Eq. (27).

A. Cross-correlation function

The definition of the cross-correlation function is based on a notion of classical periodic contour (orbit), \([q_c(t), p_c(t)]\), with the period \( T \), which approximately represents the classical periodic motion of the phase-space density. The classical periodic contour is calculated using Eqs. (35) and (36). \( q_c(t) \) is illustrated in Fig. 1.

The cross-correlation function \( X(t) \) is defined by Eqs. (34)–(38). For an illustration, we evaluate the cross-correlation function using quantum mechanics, Fig. 3. Unlike the autocorrelation function, \(|X| \) does not climb down to zero, nor creates recurrences. This property is essential for its accessibility by the classical trajectory method, which is addressed below. In the classical trajectory method, the cross-correlation function is a means to obtain the phase of the autocorrelation function at time points \( t = NT \), where the two functions coincide. These points are emphasized in both Figs. 2–3.

B. Classical trajectory calculation of cross-correlation function

The absolute value of cross-correlation function is evaluated using Eq. (40). The Wigner-Weyl transform of \( \Phi, \mathcal{P}_\Phi \), is obtained by substitution of Eq. (38) to Eq. (41),

\[
\mathcal{P}_\Phi = \frac{1}{(\hbar \pi)^F} \exp \left[ \frac{(q - q_0 + q_c(0) - q_c(t))^2}{\hbar} - \frac{(p - p_0 + p_c(0) - p_c(t))^2}{\hbar} \right].
\]

The absolute value as obtained from classical trajectory calculation is shown as part of Fig. 5. The comparison of quantum and classical results for \(|X| \) in Figs. 3 and 5, shows an excellent agreement.

The phase of the cross-correlation function \( \phi_X \) is calculated using numerical integration of the time derivative, \( \partial \phi_X / \partial t \). The time derivative of \( \phi_X \) is calculated from the integrals \( \mathcal{R}(\hat{H}) \Phi, \mathcal{R}(\hat{q}) \Phi, \) and \( \mathcal{R}(\hat{p}) \Phi \), Eq. (43). Their quantum definition is given by Eq. (44), while their WPS approximations are given by Eqs. (47). The quantum and classical results for \( \mathcal{R}(\hat{q}) \Phi \) and \( \mathcal{R}(\hat{p}) \Phi \) are displayed in Figs. 4(a) and 4(b). Clearly, the WPS approximations for \( \mathcal{R}(\hat{q}) \Phi \) and \( \mathcal{R}(\hat{p}) \Phi \) (given by lines) are in an excellent agreement with the quantum results (given by points).

Let us discuss in detail the classical approximation of the quantity \( \mathcal{R}(\hat{H}) \Phi \) in the light of the results obtained in Sec. III A. The substitution of Pullen-Edmonds Hamiltonian [Eq. (48)] to Eqs. (46) and (47), leads to the expression

\[
\mathcal{R}(\hat{H}) \Phi \approx \frac{\sum_i A_{i\mu} [q_i(t), p_i(t)] \mathcal{P}_\Phi [q_i(t), p_i(t)]}{\sum_i \mathcal{P}_\Phi [q_i(t), p_i(t)]},
\]

where \( A_{i\mu} = H + H^{(2)} \), is the sum of the classical Hamiltonian \( H \) and the quadratic term \( H^{(2)} \). The latter is given by,

FIG. 2. Autocorrelation function calculated by exact quantum propagation for the time interval \( 0 \leq t \leq 15.5 \text{ a.u.} \). The absolute value and the real part are denoted by black and gray lines, respectively. The values for \( t \in (T, 2T, 3T) \) are emphasized by dots.

FIG. 3. Cross-correlation function by quantum propagation for the time interval \( 0 \leq t \leq 15.5 \text{ a.u.} \). The absolute value and the real part are denoted by black and gray lines, respectively. The values at \( t \in [T, 2T, 3T] \), where the cross-correlation function coincides with the autocorrelation function, are emphasized.
As discussed in Sec. III A, the WPS approximation for $A H$ is not unique, and $A H$ can be substituted either by Hamiltonian only, $A H=H$, or by a series, represented here by the sum, $A H=H+H^{(2)}$. In Fig. 4(c) we show these two approximations (lines) compared with the quantum result (points). We can conclude that both approximations provide similar results, close to the quantum benchmark. The contribution of $H^{(2)}$ is relatively small due to high expectation value of energy compared to the zero-point energy.

The classical complex cross-correlation function is displayed in Fig. 5. The quantitative comparison of the quantum and classical cross-correlation functions is given in Table I, where we list the phase of the cross-correlation functions at points $t \in \{T,2T,3T\}$. $\phi_{\text{quant}}$ is the phase as obtained by quantum calculation; $\phi_{\text{class}}$ is the phase as obtained by classical calculation in the quadratic approximation, $A H=H+H^{(2)}$; and $\phi^H_{\text{class}}$ is the phase as obtained by classical calculation in the linear approximation, $A H=H$. It is clear that $\phi_{\text{class}}$ is a good approximation to $\phi_{\text{quant}}$, while the error of $\phi^H_{\text{class}}$ is very large. $\phi^H_{\text{class}}$ includes the error $\Delta \phi \sim 2 \pi$ at $t=3T$. Consequently, energy spectrum corresponding to the linear approximation includes the error $\epsilon$ estimated by, $\epsilon=\Delta \phi/(3T) \sim 0.45$ a.u. This value is close to the half of zero-point energy; this result is in agreement with the role of the quadratic term, $H^{(2)}$, in the case of harmonic oscillator, as discussed in Sec. III A.

### Table I. Phase of the cross-correlation function at points $t \in \{T,2T,3T\}$, where the cross-correlation function coincides with the autocorrelation function in regular regime. $\phi_{\text{quant}}$—exact quantum values; $\phi_{\text{class}}$—classical quadratic and linear approximations, respectively; $\epsilon_{\text{err}}$—error of the classical values, $\epsilon_{\text{err}}=|\phi_{\text{class}}-\phi_{\text{quant}}|/2 \pi$.

<table>
<thead>
<tr>
<th>$t$</th>
<th>$\phi_{\text{quant}}$</th>
<th>$\phi_{\text{class}}$</th>
<th>$\phi^H_{\text{class}}$</th>
<th>$\epsilon_{\text{err}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T=4.625$</td>
<td>$-0.226 \pi$</td>
<td>$-0.295 \pi$</td>
<td>$0.345 \pi$</td>
<td>$-0.543 \pi$</td>
</tr>
<tr>
<td>$2T=9.255$</td>
<td>$-0.428 \pi$</td>
<td>$-0.440 \pi$</td>
<td>$0.60 \pi$</td>
<td>$0.967 \pi$</td>
</tr>
<tr>
<td>$3T=13.885$</td>
<td>$-0.428 \pi$</td>
<td>$-0.602 \pi$</td>
<td>$8.70 \pi$</td>
<td>$-0.304 \pi$</td>
</tr>
</tbody>
</table>

#### C. Classical trajectory calculation of autocorrelation function

The absolute value of the autocorrelation function $|C^2(t)|$ is obtained using Eq. (8). As shown in Fig. 6, the autocorrelation function includes three recurrences, which appear in each classical period $T$. We are able to evaluate the time derivative of the phase $\dot{\phi}_c$, given by Eq. (21), using classical trajectory calculations. The phase, $\phi_c$, is evaluated from $\phi_c=\phi_c(t)/\partial t$ by numerical integration and is known for individual recurrences up to overall phase factors. To adjust the overall phase factors, it is necessary to determine the phase of the autocorrelation function for at least one time-point per

![Fig. 5. Cross-correlation function obtained by classical trajectory calculations for the time interval 0$\leq t$$\leq$11 a.u. The absolute value and the real part are denoted by black and gray lines, respectively. The points $t=NT$, which are used to obtain the phase of the autocorrelation function, are emphasized.](image)

![Fig. 6. Autocorrelation function obtained by classical trajectory calculations for the time interval 0$\leq t$$\leq$15.5 a.u. The absolute value and the real part are denoted by black and gray lines, respectively. The points $t=NT$, which are obtained from the phase of the cross-correlation function, are emphasized.](image)
three different quasiperiodic motions. At three small recurrences are found, indicating a bifurcation to the autocorrelation function, Fig. 7. The first recurrence appears for recurrences. The chaotic motion, on the other hand, is characterized by bifurcations of the phase-space density, therefore recurrences are multiplied and appear at irregular time spacing. This becomes evident after a close look at quantum trajectories with different Maslov indices (the Ehrnfest criterion is not perfectly satisfied). However, the phase error by another calculation. These points are determined by the cross-correlation function for the time points \( t = NT \), where \( \phi_\text{c}(NT) = \phi_\text{x}(NT) \), Eq. (33). The particular phase values at points \( t \in \{T, 2T, 3T\} \) are listed in Table I. Thus, the complex autocorrelation function obtained entirely from classical trajectory calculations is shown in Fig. 6.

VI. ILLUSTRATION FOR CHAOTIC REGIME

Application of the new method in chaotic regime is possible with a small modification, as shown in this section. For illustration, we use the same type of Hamiltonian [Eq. (48)], where the initial Gaussian wave packet is centered at non-zero momentum position, here we choose \( q_0 = [4 \text{ a.u.}, 1.645 \text{ a.u.}] \) and \( p_0 = [0, 4 \text{ a.u.}] \). When the corresponding phase-space packet [Eq. (27)] is propagated, its large portion occupies chaotic sea, as can be shown with the help of Poincaré surface of section, Ref. 23.

In regular regime, we could identify a quasiperiodic motion with a period \( T \), causing a sequence of equally spaced recurrences. The chaotic motion, on the other hand, is characterized by bifurcations of the phase-space density, therefore recurrences are multiplied and appear at irregular time spacing. This becomes evident after a close look at quantum autocorrelation function, Fig. 7. The first recurrence appears for \( t = 5 \text{ a.u.} \). In place of a second recurrence at \( t = 10 \text{ a.u.} \), three small recurrences are found, indicating a bifurcation to three different quasiperiodic motions. At \( t = 14 \text{ a.u.} \) there is a large recurrence, the period of which corresponds to three approximate classical periods, but the recurrence time is by 1 a.u. shorter than expected.

The bifurcations of the time-evolved phase-space density must be reflected by different periodic contours for each recurrence. The total phase of recurrences is obtained for each recurrence separately, from cross-correlation functions of their own periodic contours. Within the time interval \( 0 \leq t \leq 15.5 \text{ a.u.} \) we define five periodic contours according to Eqs. (35) and (36), with periods \( T_1, \ldots, T_5 \). The corresponding five classical cross-correlation functions are displayed in Figs. 8(a)–8(e). In Table II we list the classical and quantum phase at time points \( t \in \{T_1, \ldots, T_3\} \). It is clear that the classical calculations provide a good approximation to the chaotic autocorrelation function with the exception of the second recurrence, where the error of nearly 70% is obtained. It is assumed that this error is caused by the interference of trajectories with different Maslov indices (the Ehrnfest criterion is not perfectly satisfied). However, the phase error

<table>
<thead>
<tr>
<th>( T_1 )</th>
<th>( \phi_\text{quant} )</th>
<th>( \phi_\text{class} )</th>
<th>( err )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.32</td>
<td>0.197\pi</td>
<td>0.141\pi</td>
<td>1.87%</td>
</tr>
<tr>
<td>9.27</td>
<td>0.377\pi</td>
<td>-0.592\pi</td>
<td>68.11%</td>
</tr>
<tr>
<td>10.80</td>
<td>-0.277\pi</td>
<td>-0.427\pi</td>
<td>7.52%</td>
</tr>
<tr>
<td>11.57</td>
<td>-0.0508\pi</td>
<td>-0.164\pi</td>
<td>5.65%</td>
</tr>
<tr>
<td>14.31</td>
<td>-0.294\pi</td>
<td>-0.377\pi</td>
<td>4.16%</td>
</tr>
</tbody>
</table>
does not take a great effect in the corresponding energy spectrum due to the relatively small amplitude of the second recurrence, as shown below.

Calculation of the classical autocorrelation amplitude and time derivative of the autocorrelation phase is done according to Sec. III with no alteration for the chaotic regime. The absolute phases of individual autocorrelation recurrences are obtained from the corresponding cross-correlation functions, at points \( t \in \{ T_1, \ldots, T_3 \} \). The classical autocorrelation function for chaotic regime is shown in Fig. 9. The agreement between the classical and quantum results (Fig. 7) is remarkable.

**VII. ENERGY SPECTRUM FROM CLASSICAL AUTOCORRELATION FUNCTION**

The predominant role of the autocorrelation function in most calculations is that its Fourier transform gives energy spectra together with the corresponding Franck-Condon amplitudes \( I(E) \) as given by the equation,

\[
I(E) = \Re \left( \int_0^T dt \exp(-i\hbar E t) C(t) \right).
\]

Limitation of our method to short-time propagation allows evaluation of moderate resolved energy spectra using Eq. (52), which are shown in Figs. 10(a) and 10(b). The classical approximation is in qualitative agreement with quantum spectra in both regular and chaotic cases. The spectral interval \( 18.5 \text{ a.u.} \leq E \leq 23.5 \text{ a.u.} \) is shown in Figs. 11(a) and 11(b); we can see that the spectral peaks appear near the occupied energy levels, which are shown by vertical lines.

The actual energy levels can be obtained even from short-time propagations with the help of filter-diagonalization method. We apply the filter-diagonalization method to classical autocorrelation functions in regular and chaotic regimes in order to demonstrate the ability of the WPS approach to approximate the exact quantum energy levels.

The present implementation of the filter-diagonalization method is described below:

(i) The Fourier transforms of the time-dependent wave packet,

\[
\psi_k = \int_0^{t_{\text{max}}-\tau} dt e^{-i\hbar E_k \tau} \psi(t)
\]

are used as basis functions to find the eigenvalues of the evolution operator, \( \hat{U}(\tau) = e^{-i\hbar E_k \tau} \). \( t_{\text{max}} = 15.5 \text{ a.u.} \) is the time of the propagation, for which the autocorrelation function has been calculated; \( \tau = 0.05 \text{ a.u.} \), is a short-time interval, which gives an optimal convergence of the filter-diagonalization method. The evolution and overlap matrices are given by,

\[
U_{kk'} = \int_0^{t_{\text{max}}-\tau} dt dt' e^{i\hbar (E_k - E_k')/\hbar} C(t' - t + \tau),
\]

\[
S_{kk'} = \int_0^{t_{\text{max}}-\tau} dt dt' e^{i\hbar (E_k - E_k')/\hbar} C(t' - t).
\]

(ii) The basis functions \( \psi_k \) are defined by energy grid points \( E_k \), which are selected to follow a bell distribution around the energy window center \( E_0 \). The energy window width is given by the standard deviation \( \sigma = 1.67 \text{ a.u.} \) of energy grid points \( E_k, k = 1 \cdots 160 \). The precision of the calcu-
TABLE III. Energy levels obtained by the filter-diagonalization method from the quantum and classical short-time autocorrelation functions in regular regime. $E_{\text{class}}$—classical results; $E_{\text{quant}}$—quantum results; $\Delta$—absolute difference between quantum and classical values, $\Delta = |E_{\text{class}} - E_{\text{quant}}|$.

<table>
<thead>
<tr>
<th>$E_{\text{class}}$</th>
<th>$E_{\text{quant}}$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.0874±0.0012</td>
<td>19.0650±0.0006</td>
<td>0.0224</td>
</tr>
<tr>
<td>19.7858±0.0013</td>
<td>19.8181±0.0001</td>
<td>0.0323</td>
</tr>
<tr>
<td>20.4512±0.0016</td>
<td>20.4288±0.0015</td>
<td>0.0224</td>
</tr>
<tr>
<td>21.1399±0.0180</td>
<td>21.1651±0.0008</td>
<td>0.0252</td>
</tr>
<tr>
<td>21.8266±0.0007</td>
<td>21.8121±0.0020</td>
<td>0.0145</td>
</tr>
<tr>
<td>22.4992±0.0021</td>
<td>22.5291±0.0007</td>
<td>0.0299</td>
</tr>
<tr>
<td>23.2182±0.0025</td>
<td>23.2118±0.0014</td>
<td>0.0064</td>
</tr>
<tr>
<td>23.8771±0.0005</td>
<td>23.9074±0.0007</td>
<td>0.0303</td>
</tr>
</tbody>
</table>

TABLE IV. Energy levels obtained by the filter-diagonalization method from the quantum and classical short-time autocorrelation functions in chaotic regime. $E_{\text{class}}$—classical results; $E_{\text{quant}}$—quantum results; $\Delta$—absolute difference between quantum and classical values, $\Delta = |E_{\text{class}} - E_{\text{quant}}|$.

<table>
<thead>
<tr>
<th>$E_{\text{class}}$</th>
<th>$E_{\text{quant}}$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.575±0.015</td>
<td>18.557±0.022</td>
<td>0.018</td>
</tr>
<tr>
<td>18.924±0.016</td>
<td>18.894±0.027</td>
<td>0.031</td>
</tr>
<tr>
<td>19.361±0.025</td>
<td>19.328±0.036</td>
<td>0.032</td>
</tr>
<tr>
<td>19.807±0.020</td>
<td>19.778±0.041</td>
<td>0.029</td>
</tr>
<tr>
<td>20.248±0.003</td>
<td>20.212±0.024</td>
<td>0.037</td>
</tr>
<tr>
<td>20.708±0.015</td>
<td>20.700±0.014</td>
<td>0.008</td>
</tr>
<tr>
<td>21.123±0.015</td>
<td>21.103±0.005</td>
<td>0.020</td>
</tr>
<tr>
<td>21.530±0.017</td>
<td>21.519±0.025</td>
<td>0.011</td>
</tr>
<tr>
<td>22.010±0.027</td>
<td>21.999±0.026</td>
<td>0.010</td>
</tr>
<tr>
<td>22.406±0.019</td>
<td>22.386±0.027</td>
<td>0.020</td>
</tr>
<tr>
<td>22.830±0.023</td>
<td>22.814±0.028</td>
<td>0.016</td>
</tr>
<tr>
<td>23.307±0.021</td>
<td>23.309±0.018</td>
<td>0.002</td>
</tr>
</tbody>
</table>

The lost phase factors are obtained by calculation of a cross-products of expectation values. We suggest a method to overcome a problem of lost overall phases of separate recurrence of Hamiltonian due to short-time propagation. It is thus characteristic that the standard error of the obtained energy levels is almost one order of magnitude larger in chaotic case compared to regular regime.

**VIII. CONCLUSIONS**

We propose a quasiclassical method for calculation of complex autocorrelation functions within Ehrenfest time limit. The method is tested for a model of two nonlinearly coupled harmonic oscillators for regular and chaotic regimes, and proves to work in good quantitative agreement with quantum benchmarks.

We formulate an approximation of complex autocorrelation function which is fully consistent with the Wigner phase-space approach, namely, uses the rigorous quasiclassical expression for expectation values. We suggest a way to overcome a problem of lost overall phases of separate recurrences, which arise using the presented method (Ref. 23). The lost phase factors are obtained by calculation of a cross-correlation function which serves as a link between $t=0$ and $t=T$, where $T$ is the approximate classical period.

Using the approximate complex autocorrelation function we attempt to calculate the energy spectrum of the system with the help of filter-diagonalization method. We demonstrate that the Wigner phase-space approach is capable of prediction of energy levels of the given nonlinear system in regular regime with a very good precision.

One of the main obstacles for practical application of the Wigner phase-space method, and one of the main challenges of this approach can be expressed in words of Garashchuk and Tannor. \(^21\) “Although we have been able to calculate the phase to the same accuracy as the amplitude, in our experience the method is accurate only through intermediate times; without further modification the classical Wigner method is not competitive with methods based on the VVG (van Vleck-Gutzwiller propagator) expression.” (Italics added.) The solution may hint toward separation of autocorrelation recur-
rences using the calculation of their Maslov index; the preliminary discussion of this problem is found in Ref. 23.

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