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Semiclassical Moyal dynamics

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We present a semiclassical Moyal dynamics (SMD) method based on the phase space formulation of quantum dynamics. In contrast to the quantized Hamiltonian dynamics approach by Prezhdo *et al.* using the Heisenberg equation of motion, SMD adopts the Moyal equation of motion to derive the time evolution of expectation values and uses an auxiliary phase space distribution technique to systematically terminate the coupled equations of motion. Thereby, tedious derivation of commutators is essentially not required, and semiclassical dynamics of arbitrary orders can be realized. The appealing simplicity, flexibility, and reliability of SMD are demonstrated in three representative model systems with strong quantum effects. *Published by AIP Publishing.* https://doi.org/10.1063/1.5067005

I. INTRODUCTION

Molecular dynamics (MD) has been a powerful tool to investigate the dynamical properties of a wide range of systems in chemistry, physics, biology, and material sciences.[1–4] The simplicity and high efficiency of MD, however, come with a trade-off in accuracy when quantum effects (e.g., tunneling, state branching, decoherence, and zero-point energy) are significant. In contrast, quantum mechanics provides an exact solution to these problems but is usually limited to small systems due to the complexity and high computational cost.[5–7] Thereby, developing semiclassical and mixed quantum-classical approaches with a good balance of accuracy and efficiency has become a subject of great interest in the past decades.[8–20]

In 2000, Prezhdo and Pereverzev proposed the quantized Hamiltonian dynamics (QHD) approach for semiclassical dynamics.[21] Using the Heisenberg formulation of quantum dynamics, they obtain an infinite hierarchy of equations for the time evolution of observables. Truncation of the hierarchy gives different levels of approximations to the exact quantum dynamics. Namely, the first-order QHD (QHD-1) is equivalent to the classical Hamiltonian dynamics, while quantum effects are naturally considered when higher order terms are included. QHD has been applied to a variety of problems, e.g., the vibrational frequency analysis of molecules,[22] the tunneling escape from a metastable state,[23] the interference pattern in double-slit experiments,[24] the energy flow between vibrational modes,[25] the discrete breathers in nonlinear coupled systems,[26] the vibrational coherence transfer in molecular dimers,[27] the population transfer in electron-phonon coupled systems,[28] and the charge transport in organics at low temperatures.[29] QHD has shown its capability to describe different quantum effects with modest computational cost.

On the basis of QHD, some variant methods have been developed. In the quantized mean-field (QMF) approach,[30,31] the system is divided into the quantum and semiclassical parts, which are characterized by the Schrödinger equation and QHD, respectively. The interaction between the two subsystems is described in a mean field manner for nonadiabatic dynamics. The quantal cumulant dynamics (QCD) approach by Shigeta and co-workers utilizes the position shift operator and cumulant expansion techniques in the derivations.[32,33] As an extension of QHD,[34,35] QCD shows better conservation of energy and has been demonstrated in a number of applications,[36] e.g., the quantum confinement under a magnetic field[37] and the structure optimization of quantum Morse clusters.[38] Recently, Smith and Akimov proposed the entangled trajectories Hamiltonian dynamics (ETHD) method, which reformulates the classically mapped second-order QHD (QHD-2) with coupled classical trajectories.[39] ETHD shows remarkable agreement with fully quantum results in several testing models.

Despite the great success, QHD and its variant approaches have several intrinsic difficulties. Namely, the derivation of the equations of motion requires tedious calculation of commutators, and thus high order QHD simulations are difficult to carry out.[21,32] Especially, Weyl symmetrization[40] should be applied to cross terms of position and momentum operators, and thus it further increases the complexity of the derivations. Furthermore, closure approximations are required to approximate high-order variables in terms of low-order terms, and again a general closure is difficult to achieve based on operators. In the literature, only decomposition formulas for averages up to the fifth order have been given, and only the second, third, and fourth order QHD have been utilized so far.[10,23] As the lowest order incorporating quantum effects, QHD-2 has been the most popular choice in previous studies. Actually, QHD-2 can be mapped onto classical mechanics by doubling the dimensionality[41–43] and is closely related to the thawed Gaussian wave packet dynamics.[10,43–46] In general situations, a proper description of the dynamics may require high order semiclassical solutions, which have not been extensively studied yet.

In this study, we propose a novel semiclassical Moyal dynamics (SMD) framework to give a general description of

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semiclassical dynamics of arbitrary orders. In the phase space formulation, we derive general expressions for the equations of motion and introduce an auxiliary phase space distribution technique, which gives general closures for the coupled equations of motion. As examples, SMD is applied to study (1) the decay dynamics from a metastable cubic potential, (2) the oscillation in a Morse potential, and (3) the barrier crossing in a double well potential.

II. THEORY

A. Phase space formulation of quantum dynamics

For a system with general Hamiltonian $\hat{H}$, the time evolution of any observable $\hat{A}$ follows the standard Heisenberg equation of motion

$$\frac{d}{dt}\hat{A}_H = \left(\frac{\partial \hat{A}}{\partial t}\right)_H + \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}\right], \tag{1}$$

where the subscript H indicates operators in the Heisenberg picture, $\hbar$ is the reduced Planck constant, and $[\cdot,\cdot]$ denotes the commutator of two operators. Taking the expectation values on both sides of Eq. (1), one obtains

$$\frac{d}{dt}\left\langle \hat{A}\right\rangle = \left\langle \frac{\partial \hat{A}}{\partial t}\right\rangle + \frac{1}{i\hbar}\left\langle \left[\hat{A}, \hat{H}\right]\right\rangle. \tag{2}$$

Switching from the Hilbert space operator representation to the equivalent phase space representation[47–50] yields the Moyal equation of motion

$$\frac{d}{dt}\langle A\rangle = \left\langle \frac{\partial A}{\partial t}\right\rangle + \langle\{\{A, H\}\}\rangle. \tag{3}$$

Here, A and H are the real-valued functions of coordinates and momenta, which are phase space counterparts to the corresponding quantum mechanical operators $\hat{A}$ and $\hat{H}$. $\langle A\rangle$ is the average value of A weighted by the phase space distribution, taking the place of $\left\langle \hat{A}\right\rangle$ to describe the expectation value. $\{\{\cdot,\cdot\}\}$ is the Moyal bracket defined as

$$\{\{f, g\}\} = \frac{2}{\hbar} f \sin\left[\frac{\hbar}{2}\left(\sum_i \overleftarrow{\partial}_{q_i}\overrightarrow{\partial}_{p_i} - \overleftarrow{\partial}_{p_i}\overrightarrow{\partial}_{q_i}\right)\right] g, \tag{4}$$

where f and g are the phase space functions, the index i runs over all degrees of freedom with coordinates $\{q_i\}$ and momenta $\{p_i\}$, and the left and right arrows denote the left and right partial derivatives, respectively.

For the sake of simplicity and without loss of generality, we consider the Hamiltonian with only one degree of freedom

$$H = \frac{p^2}{2m} + V(q), \tag{5}$$

where m is the mass of the particle. Substituting Eq. (5) into Eq. (3), we obtain

$$\frac{d}{dt}\langle A\rangle = \left\langle \frac{\partial A}{\partial t}\right\rangle + \langle\{A, H\}\rangle + \sum_{k=1}^{\infty} \frac{(-1)^{k+1}\hbar^{2k}}{(2k+1)!2^{2k}}\left\langle A_p^{(2k+1)} V_q^{(2k+1)}\right\rangle, \tag{6}$$

where we have used the abbreviations $A_p^{(i)} = \partial^i A/\partial p^i$ and $V_q^{(i)} = \partial^i V/\partial q^i$. $\{\cdot,\cdot\}$ is the Poisson bracket defined as

$$\{f, g\} = \frac{\partial f}{\partial q}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial q}. \tag{7}$$

Apparently, $\hbar$ only exists in the third term on the right-hand side of Eq. (6), which is non-zero only when the corresponding partial derivatives of A and V exist.

B. Coupled equations of motion for phase space averages

Replacing A in Eq. (6) with different phase space variables yields first-order differential equations for time evolution. For instance, setting $A = q$ and p, we obtain

$$\frac{d}{dt}\langle q\rangle = \frac{1}{m}\langle p\rangle, \tag{8}$$

$$\frac{d}{dt}\langle p\rangle = -\left\langle V_q^{(1)}\right\rangle, \tag{9}$$

which are known as the Ehrenfest theorem. Note that similar equations are normally derived based on the expectation values of the corresponding operators by Eq. (2). To get a closed system of equations, we generally need to continue to calculate the time derivative of $\left\langle V_q^{(1)}\right\rangle$

$$\frac{d}{dt}\left\langle V_q^{(1)}\right\rangle = \frac{1}{m}\left\langle V_q^{(2)} p\right\rangle, \tag{10}$$

which further depends on $\left\langle V_q^{(2)} p\right\rangle$. The corresponding equation is

$$\frac{d}{dt}\left\langle V_q^{(2)} p\right\rangle = \frac{\left\langle V_q^{(3)} p^2\right\rangle}{m} - \left\langle V_q^{(1)} V_q^{(2)}\right\rangle. \tag{11}$$

These derivations of time derivatives can be repeated and, in general, results in an infinite system of coupled equations of motion. Note that the variables in Eqs. (8)–(11) share some similarities with the direct variables suggested by Akimov and Prezhdo.[51]

To derive general expressions for the equations of motion, we assume that the potential energy surface can be approximately expressed as a polynomial function of degree M

$$V(q) = \sum_{k=0}^{M} a_k q^k, \tag{12}$$

where a_k are the coefficients. This can be done, for instance, through Taylor expansion of the potential around a fixed point or around the moving instantaneous position.[25] In practice, some systems may require a very large M to achieve a satisfied description. Nevertheless, we hereby illustrate our approach by deriving equations of motion for systems whose potentials can be cast into the form in Eq. (12). It is straightforward that the variables in the coupled equations of motion in Eqs. (8)–(11) become linear combinations of $\{q^i p^j\}$, which can be classified into different orders. The first-order variables are q and p, whose equations of motion have been given by Eqs. (8) and (9), respectively. For second-order variables (i.e., q^2, qp, and p^2), inserting Eq. (12) into Eq. (6) yields

$$\frac{d}{dt}\langle q^2\rangle = \frac{2}{m}\langle qp\rangle, \tag{13}$$

$$\frac{d}{dt}\langle qp\rangle = \frac{\langle p^2\rangle}{m} - \sum_{k=1}^{M} k a_k \langle q^k\rangle, \tag{14}$$

$$\frac{d}{dt}\langle p^2\rangle = -2\sum_{k=1}^{M} k a_k \langle q^{k-1}p\rangle. \tag{15}$$

In general, there exist $N+1$ variables for the Nth order. From Eqs. (14) and (15), second-order averages are coupled with higher-order averages when $M > 2$. The same conclusion also holds for averages with order $N > 2$.

Different sets of phase space variables can be adopted to construct the coupled equations of motion. Prezhdo has shown that reduced second-order variables can be defined relative to the instantaneous values of the averaged coordinate and momentum to obtain simplified equations of motion.[41] Inspired by this, we choose $\mu_q = \langle q\rangle$, $\mu_p = \langle p\rangle$, $\sigma_q = \sqrt{\langle (q-\mu_q)^2\rangle}$, and $\sigma_p = \sqrt{\langle (p-\mu_p)^2\rangle}$ and define the dimensionless coordinate and momentum as $\tilde{q} = (q-\mu_q)/\sigma_q$ and $\tilde{p} = (p-\mu_p)/\sigma_p$, which are convenient for numerical calculations. Then $\tilde{q}^i\tilde{p}^j$ can be used to replace q^ip^j. The averages, $\xi_{ij} = \langle \tilde{q}^i\tilde{p}^j\rangle$, have properties $\xi_{00} = 1$, $\xi_{10} = \xi_{01} = 0$, and $\xi_{20} = \xi_{02} = 1$. From Eq. (12), we can express V as polynomial series of $\tilde{q}$

$$V(\tilde{q}) = \sum_{k=0}^{M} b_k \tilde{q}^k, \tag{16}$$

where $b_k = \sum_{l=k}^{M} C_l^k \mu_q^{l-k}\sigma_q^k a_l$ and $C_m^n = m!/[n!(m-n)!]$. Appling Eq. (16) to Eq. (6) yields a complete set of coupled equations of motion

$$\frac{d}{dt}\mu_q = \frac{\mu_p}{m}, \tag{17}$$

$$\frac{d}{dt}\mu_p = \lambda, \tag{18}$$

$$\frac{d}{dt}\sigma_q = \frac{\sigma_p\xi_{11}}{m}, \tag{19}$$

$$\frac{d}{dt}\sigma_p = \chi, \tag{20}$$

$$\frac{d}{dt}\xi_{ij} = \alpha\xi_{ij} + \beta\xi_{i-1,j+1} + \gamma\xi_{i,j-1} + \sum_{k=0}^{K}\sum_{l=2k+1}^{M}\eta_{kl}\xi_{i-2k-1+l,j-2k-1}, \tag{21}$$

where we have introduced symbols $\alpha = -ij\chi/\sigma_p - i\xi_{11}\sigma_p/(m\sigma_q)$, $\beta = i\sigma_p/(m\sigma_q)$, $\gamma = -ij\lambda/\sigma_p$, $\eta_{kl} = (-1)^{k+1}b_l\hbar^{2k}C_j^{2k+1}A_l^{2k+1}/(2^{2k}\sigma_p^{2k+1}\sigma_q^{2k+1})$, $\lambda = -\sum_{k=1}^{M} k b_k \xi_{k-1,0}/\sigma_q$, $\chi = -\sum_{k=1}^{M} k b_k \xi_{k-1,1}/\sigma_q$, and $A_m^n = m!/(m-n)!$ to simplify the expressions, and K is the largest integer no greater than $(\min\{j, M\} - 1)/2$. From Eq. (21), we can find that any variable ξ_{ij} with order $i+j$ relies on other ξ_{kl}, whose highest order is $i+j+M-2$.

C. Closure of the equations of motion

For polynomial potentials of degree $M > 2$, the infinite coupled equations of motion need to be terminated by approximating higher-order averages via lower-order averages. Here, we consider variables up to the Nth order for time evolution through Eqs. (17)–(21) and introduce an auxiliary phase space distribution, $P_N(q,p)$, to make the closure. Our idea is to obtain $P_N(q,p)$ based on lower-order averages and then use $P_N(q,p)$ to calculate high-order averages approximately. In general, we can express $P_N(q,p)$ as a linear expansion

$$P_N(q,p) = \sum_{0\le k+l\le N} c_{kl} f_{kl}(q,p), \tag{22}$$

where $\{f_{kl}(q,p)\}$ are the basis functions and $\{c_{kl}\}$ are the corresponding coefficients. Then, for each ξ_{ij}, we have the following equation:

$$\xi_{ij} = \sum_{0\le k+l\le N} M_{ij,kl} c_{kl}, \tag{23}$$

where $M_{ij,kl} = \int f_{kl}(q,p)\tilde{q}^i\tilde{p}^j dqdp$. For Nth-order SMD (SMD-N), ξ_{ij} with $0 \le i+j \le N$ are known, and the number of linear equations from Eq. (23) is $(N+1)(N+2)/2$, which is exactly the same as the number of coefficients in Eq. (22). Solving this system of linear equations gives $\{c_{kl}\}$. Then ξ_{ij} with $i+j > N$ can be approximately evaluated with these coefficients through Eq. (23) and used to calculate the time derivatives of ξ_{ij} with $i+j \le N$ by Eq. (21).

The basis functions in Eq. (22) may have different forms. Inspired by the eigenstates of harmonic oscillators, we hereby choose a Gaussian-type basis

$$f_{kl}(q,p) = f(q,p)\tilde{q}^k\tilde{p}^l, \tag{24}$$

where $f(q,p) = \exp\{-[(q-\mu_q)^2/\sigma_q^2 - 2\rho(q-\mu_q)(p-\mu_p)/(\sigma_q\sigma_p) + (p-\mu_p)^2/\sigma_p^2]/[2(1-\rho^2)]\}/[2\pi\sigma_q\sigma_p(1-\rho^2)^{1/2}]$ is set as the standard bivariate normal distribution with correlation coefficient $\rho = \xi_{11}$. Then the matrix elements in Eq. (23) become $M_{ij,kl} = \int f(q,p)\tilde{q}^{i+k}\tilde{p}^{j+l}dqdp$, which can be evaluated based on Wick's theorem. Namely, if $i+j+k+l$ is odd, $M_{ij,kl}$ is always zero; otherwise, we have

$$M_{ij,kl} = \sum_{n=0}^{I} \rho^{a-2n} C_a^{2n} A_b^{a-2n} (2n-1)!!(b-a+2n-1)!!, \tag{25}$$

which relies only on $a = \min\{i+k, j+l\}$ and $b = \max\{i+k, j+l\}$. I is the largest integer no greater than $a/2$. As a result, we can decompose the $(N+1)(N+2)/2$ linear equations in Eq. (23) into two subsystems: one with odd $i+j$ and $k+l$, and the other one with even $i+j$ and $k+l$.

D. Algorithm of SMD

Using one-dimensional systems with polynomial potentials of degree M as examples, we give a step-by-step outline of our N-order SMD algorithm for semiclassical dynamics as follows:

(1) At time zero, we set the wave function, $\psi(q)$, according to the problem under investigation. The initial variables (i.e., μ_q, μ_p, σ_q, σ_p, ρ, and $\{\xi_{ij}\}$ with $3 \le i+j \le N$) are then calculated accordingly. For the case of a Gaussian wave packet,

$$\psi(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega(q-q_0)^2}{2\hbar} + i\frac{p_0 q}{\hbar}\right]. \tag{26}$$

Through Wigner transform, we obtain the corresponding phase space distribution as $P(q,p) = \exp\{-[(q-\mu_q)^2/(2\sigma_q^2) + (p-\mu_p)^2/(2\sigma_p^2)]\}/(2\pi\sigma_q\sigma_p)$. Then, we can easily calculate the phase space averages $\mu_q = q_0$, $\mu_p = p_0$, $\sigma_q = \sqrt{\hbar/(2m\omega)}$, $\rho = 0$, and $\sigma_p = \sqrt{m\hbar\omega/2}$. When both i and j are even, $\xi_{ij} = (i-1)!!(j-1)!!$; otherwise, $\xi_{ij} = 0$ at $t = 0$.

(2) At each time step t, we calculate the SMD variables after a time interval dt through solving Eqs. (17)–(21) with the fourth-order Runge-Kutta algorithm. To this end, we first calculate the matrix elements $M_{ij,kl}$. For the basis functions defined by Eq. (24), $M_{ij,kl}$ follows Eq. (25) if $i+j+k+l$ is an even number and $M_{ij,kl}$ is zero in other cases. Solving the linear equations given by Eq. (23) with $0 \le i+j \le N$, we get the coefficients $\{c_{kl}\}$ and the auxiliary phase space distribution, $P_N(q,p)$. Then we evaluate $\{\xi_{ij}\}$ with $N+1 \le i+j \le N+M-2$ approximately through Eq. (23) and plug their values into the right-hand sides of Eqs. (17)–(21) to obtain closed differential equations. This step is repeated until a certain predefined criterion is achieved.

(3) For any observable $A(p,q)$, the time evolution of the expectation value is achieved based on the time-dependent auxiliary phase space distribution

$$\langle A(p,q,t)\rangle = \int A(p,q)P_N(x,p,t)dqdp. \tag{27}$$

Thereby, a complete description of the semiclassical dynamics is achieved based on the time evolution of only a certain number of averages.

E. Relation between SMD and QHD

The same as QHD-1, SMD-1 gives Hamilton's equations of motion for classical mechanics (see Appendix A). For SMD-2, Eq. (23) reduces to an odd and an even subsystem of linear equations

$$\begin{bmatrix} 1 & \rho \\ \rho & 1 \end{bmatrix}\begin{bmatrix} c_{10} \\ c_{01} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \tag{28}$$

$$\begin{bmatrix} 1 & 1 & 1 & \rho \\ 1 & 3 & 1+2\rho^2 & 3\rho \\ 1 & 1+2\rho^2 & 3 & 3\rho \\ \rho & 3\rho & 3\rho & 1+2\rho^2 \end{bmatrix}\begin{bmatrix} c_{00} \\ c_{20} \\ c_{02} \\ c_{11} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ \rho \end{bmatrix}. \tag{29}$$

The solution is $c_{00} = 1$ and $c_{10} = c_{01} = c_{20} = c_{02} = c_{11} = 0$, which gives a phase space distribution equivalent to that in the second order QCD.[35] From Eq. (23), the SMD closure becomes $\xi_{ij} \approx M_{ij,00}$. Thereby, $\xi_{04} = \xi_{40} \approx 3$, $\xi_{22} \approx 1+2\rho^2$, and $\xi_{13} = \xi_{31} \approx 3\rho$, while all third- and fifth-order averages are zero. In comparison, the closure scheme of QHD also ensures that the third- and fifth-order $\langle \tilde{q}^i\tilde{p}^j\rangle$ averages are zero because $\langle\tilde{q}\rangle = 0$ and $\langle\tilde{p}\rangle = 0$ (see Appendix B). According to Eq. (B17), the fourth-order averages in QHD are approximated as $\langle\tilde{p}^4\rangle \approx 3\langle\tilde{p}^2\rangle\langle\tilde{p}^2\rangle = 3$, $\langle\tilde{q}^4\rangle \approx 3\langle\tilde{q}^2\rangle\langle\tilde{q}^2\rangle = 3$, $\langle\tilde{q}^2\tilde{p}^2\rangle \approx \langle\tilde{q}^2\rangle\langle\tilde{p}^2\rangle + 2\langle\tilde{q}\tilde{p}\rangle\langle\tilde{q}\tilde{p}\rangle = 1+2\rho^2$, $\langle\tilde{q}\tilde{p}^3\rangle \approx 3\langle\tilde{q}\tilde{p}\rangle\langle\tilde{p}^2\rangle = 3\rho$, and $\langle\tilde{q}^3\tilde{p}\rangle \approx 3\langle\tilde{q}^2\rangle\langle\tilde{q}\tilde{p}\rangle = 3\rho$, which are also the same as our closures in phase space. Actually, we have carefully checked closure formulas for variables up to the fifth order in SMD-3 and SMD-4. Our closure scheme using Eqs. (22) and (24) always reproduces the QHD closure proposed by Prezhdo *et al.*[21,23] Note that higher-order QHD closures have not been given in the literature due to the complex decomposition formulas (see Appendix B). In phase space, the closure of arbitrary order can be easily realized as discussed above. Thereby, the present SMD approach gives a proper description of the quantized Hamiltonian dynamics.

III. RESULTS AND DISCUSSION

The SMD approach is applied to three one-dimensional model systems, which possess different potential energy surfaces: (A) a cubic potential, (B) a Morse potential, and (C) a double well potential. Model A is a well-studied system in the literature,[23] where the quantum tunneling effect plays an important role. Here, we use it to benchmark our SMD algorithm using previous QHD results as references. Models B and C are more complex systems, where we can truncate terms higher than the fifth order to get a better description of the dynamics. In these two models, the SMD results are compared with the exact quantum dynamics by the discrete variable representation (DVR) method.[5] The time step of DVR is chosen as the reciprocal of the spectral radii of the Hamiltonian matrix.[52] In the following calculations, atomic units are adopted unless otherwise noted.

A. Decay from a metastable cubic potential

The first model under investigation is a cubic potential[23]

$$V(q) = q^2/2 + q^3/6, \tag{30}$$

which mimics the tunneling escape of an electron from a metastable state. The mass is $m = 1$. At the vicinity of $q = 0$, it can be approximated by the harmonic potential $V(q) = q^2/2$ in which the ground state is taken as the initial wave function

$$\psi(q) = \pi^{-1/4}\exp\left(-q^2/2\right). \tag{31}$$

The potential energy surface and the initial spatial distribution of the electron are shown in Fig. 1(a). By design, the metastable state can decay only by tunneling. This model has been extensively studied by Prezhdo and Pahl previously.[23] It has been shown that increasing the order from two to four leads to a systematic improvement of the QHD descriptions. In Fig. 1(b), we show the numerical results of SMD. A time interval of 0.1 a.u. is adopted to get converged results. The closure is based on the auxiliary phase space distribution in Eqs. (22) and (24). Apparently, SMD with this closure scheme reproduces exactly the QHD results when the same order is used.

B. Oscillation in a Morse potential

The second model is a Morse potential [see Fig. 2(a)][51]

$$V(q) = a[\exp(-2bq) - 2\exp(-bq)], \tag{32}$$

with $a = 4.419$ eV, $b = 2.567$ Å^{-1}, and $m = 1836$. It was designed to describe the anharmonic stretching of the O-H bond in water.[53] Similar to model A, the initial wave

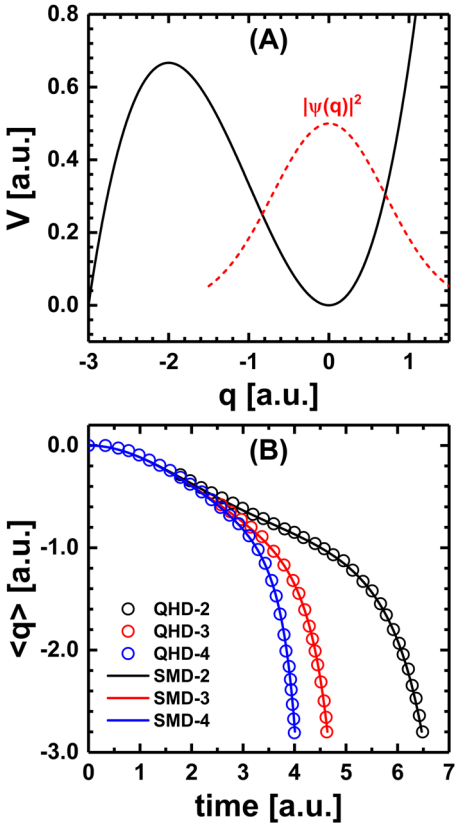

FIG. 1. (a) Potential energy surface of the cubic potential model (black line) and a sketch of the initial Gaussian wave packet (red dashed line) and (b) trajectory of the metastable particle calculated by QHD and SMD with different orders as indicated.

function is taken as the ground state of the harmonic potential approximated at the minimum of the potential (i.e., $q = 0$). To treat this non-polynomial potential, we follow the fixed-frame approximation proposed by Prezhdo and Pereverzev.[25] Namely, we expand the Morse potential with Taylor series

$$V(q) \approx \sum_{n=0}^{M} \frac{1}{n!} V_q^{(n)}(0) q^n, \tag{33}$$

where $V_q^{(n)}$ is the nth derivative of the potential with respect to the coordinate. A better description of the potential is achieved when a larger M is adopted.

In Figs. 2(b) and 2(c), we show the time evolution of the average coordinate and the average momentum with SMD-2. Compared with model A, the larger mass here allows us to use a larger time interval of $dt = 10$ a.u. to simulate the dynamics. As a reference, the DVR result is achieved with a grid spacing of 0.01 within $[-0.76, 2.00]$. We can find that a systematic improvement of the results is achieved with increasing M. SMD-2 with $M = 6$ is more or less converged and gives a good approximation of the quantum-mechanical result by DVR. We know that the highest order of the dimensionless variables to be truncated is $N + M - 2$ for SMD-N with a polynomial potential of degree M. Thereby, the highest order to be truncated here is six, which goes beyond the fifth-order closure scheme available in the literature (see Appendix B). In contrast, the present SMD approach gives a satisfactory description of the dynamics. In Figs. 2(b) and 2(c), we also

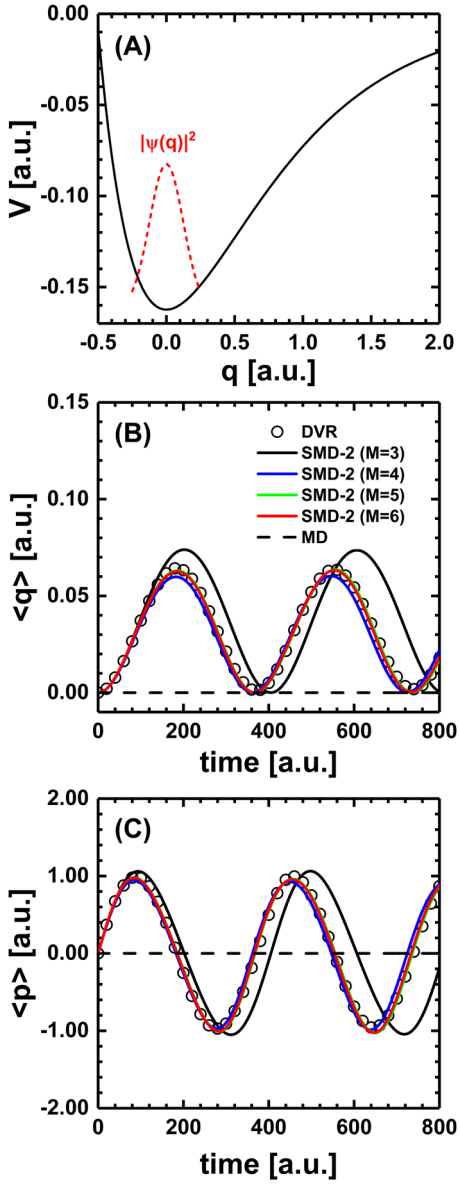

FIG. 2. (a) Potential energy surface of the Morse potential model (black line) and a sketch of the initial Gaussian wave packet (red dashed line), and time evolution of the average (b) position and (c) momentum computed by SMD-2 using different Taylor expansions of the potential. M is the order of the Taylor expansion. Exact quantum results by DVR and classical MD results are shown as open circles and dashed lines, respectively.

show the results of classical MD. Due to our choice of the initial condition, the particle is frozen during the dynamics. Thereby, the dynamics in this model is completely due to quantum effects.

C. Barrier crossing in a double well potential

In the third model, we consider a symmetric double well potential [see Fig. 3(a)]

$$V(q) = aq^2 + bq^4, \tag{34}$$

with $a = -3 \times 10^{-4}$, $b = 2.4 \times 10^{-5}$, and $m = 1836$. By design, the barrier is about $k_B T$, where k_B is the Boltzmann constant and T is the room temperature. The distance between the two local minima is 5 a.u., which is a typical intermolecular

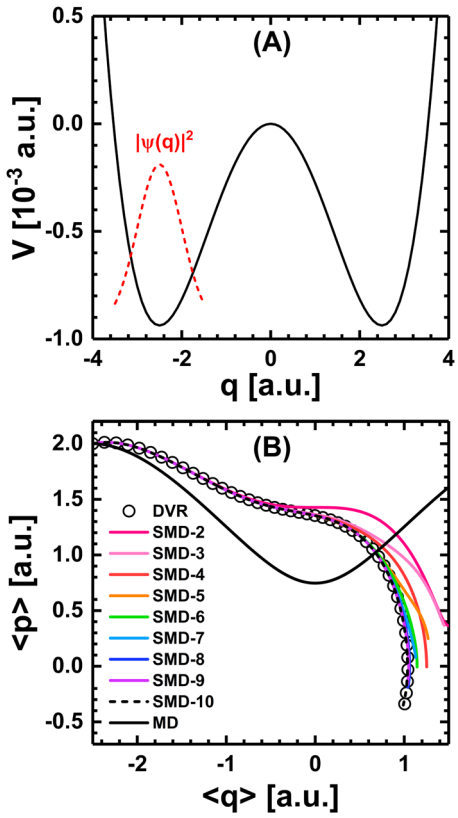

FIG. 3. (a) Potential energy surface of the double well potential model (black line) and a sketch of the initial Gaussian wave packet (red dashed line), and (b) phase space trajectories computed by DVR, classical MD, and SMD with different orders as indicated.

distance. The initial wave function is a Gaussian wave packet located at the left well minimum

$$\psi(q) = (2\pi d)^{-1/4} \exp\left[-(q-q_0)^2/(4d) + ip_0 q\right], \qquad (35)$$

where $d = 0.25$, $q_0 = -2.5$, and $p_0 = 2$. In the DVR calculation, we consider a grid spacing of 0.05 within $[-10, 10]$. In Fig. 3(b), we investigate the phase space trajectories of SMD with $dt = 10$ a.u. Increasing the SMD order leads to a systematic convergence of the trajectory, and SMD-10 reproduces the DVR result quantitatively. In this model, the highest order of the variables to be truncated is twelve, which is very difficult to realize with the traditional approaches in Hilbert space. In comparison, the classical MD results deviate strongly with the quantum solutions [see Fig. 3(b)]. To provide more insightful assessment of SMD, we further investigate the time evolution of second-order variables (see Fig. 4). Again, SMD results systematically converge to the exact quantum solutions with increasing order in all cases.

Finally, we point out that SMD provides a flexible theoretical framework to study semiclassical dynamics. In the present study, we consider dimensionless variables, linear expansion of the auxiliary phase space distribution, and a specific set of Gaussian-type basis functions to illustrate the capability of SMD. Low-order SMD with these choices reproduces the results of the traditional QHD. The SMD framework, however, gives us great flexibility to tune the variable set for time evolution and the form of the auxiliary phase space distribution to make closures. Thereby, SMD has the potential to go

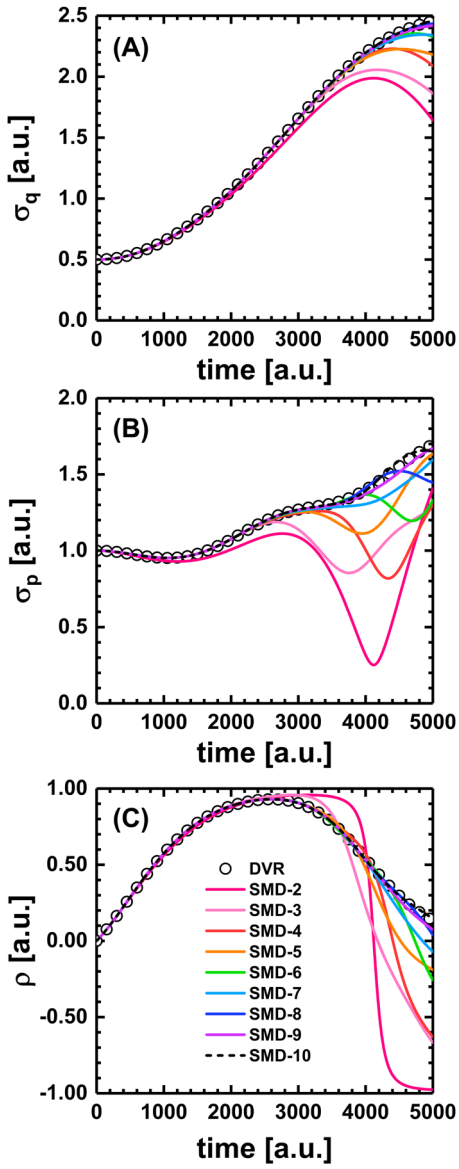

FIG. 4. Time evolution of the second-order variables (a) σ_q, (b) σ_p, and (c) ρ for the double well potential model. The results of DVR and SMD with different orders are compared.

beyond existing average-based approaches when dealing with complex dynamics. Besides, we hereby use one-dimensional polynomial potentials as examples to describe the algorithm of SMD. General potentials can be also investigated in a similar way. The computational cost may grow significantly with the dimension due to the larger number of variables, and thus efficient algorithms are needed. The initial condition may also have a strong impact on the dynamics.[54] When a thermostat is considered, a simple quantum initial condition can be used for harmonic oscillators.[29] Relevant studies are currently under way.

IV. CONCLUSION

In summary, we have extended the traditional QHD method to the phase space formulation. The resulting SMD approach for semiclassical dynamics has shown significant advantages in simplicity, generality, and flexibility. The tedious

Weyl symmetrization and operator algebras for the equations of motion have been avoided, and a systematic closure scheme has been proposed. We have adopted a specific set of variables and auxiliary phase space distribution to illustrate the capability of SMD. Using three model systems as examples, we have shown that low-order SMD reproduces the results of QHD, while high-order SMD systematically converges to the exact quantum dynamics by DVR. Thereby, SMD provides a fundamental platform to develop better approaches for semiclassical and mixed quantum-classical dynamics in the future.

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APPENDIX A: FIRST-ORDER SMD AND HAMILTONIAN DYNAMICS

In SMD-1, the variable set contains only μ_q and μ_p, which are the average values of q and p, respectively. The corresponding equations of motion are given by Eqs. (17) and (18). The time derivative of μ_p is $\lambda = -\sum_{k=1}^{M}\sum_{l=k}^{M} kC_l^k \mu_q^{l-k}\sigma_q^{k-1}a_l\xi_{k-1,0}$. In the classical limit, $\sigma_q \to 0$ and thus k in the sum must be 1. We have $\lambda \to -\sum_{l=1}^{M} l\mu_q^{l-1}a_l$, which equals to $-V'(\mu_q)$. Then the equations of motion for SMD-1 read

$$\frac{d}{dt}\mu_q = \frac{\mu_p}{m}, \tag{A1}$$

$$\frac{d}{dt}\mu_p = -V'(\mu_q), \tag{A2}$$

which reproduce Hamilton's equations of motion for classical mechanics

$$\frac{d}{dt}\mu_q = \frac{\partial H}{\partial \mu_p}, \tag{A3}$$

$$\frac{d}{dt}\mu_p = -\frac{\partial H}{\partial \mu_q}, \tag{A4}$$

with Hamiltonian $H = \mu_p^2/2m + V(\mu_q)$. For higher-order SMD, the Hamiltonian dynamics is quantized by coupling to other variables arising from quantum mechanics.

APPENDIX B: AVAILABLE CLOSURE SCHEMES OF QHD

In QHD, the third, fourth, and fifth order averages are generally decomposed into[21,23]

$$\langle ABC\rangle \approx I_{21} - 2I_{111}, \tag{B1}$$

$$\langle ABCD\rangle \approx I_{31} + I_{22} - 2I_{211} + 6I_{1111}, \tag{B2}$$

$$\langle ABCDE\rangle \approx I_{41} + I_{32} - 2I_{311} - 2I_{221} + 6I_{2111} - 24I_{11111}, \tag{B3}$$

where the decomposition terms are defined as

$$I_{21} = \langle AB\rangle\langle C\rangle + \langle AC\rangle\langle B\rangle + \langle BC\rangle\langle A\rangle, \tag{B4}$$

$$I_{111} = \langle A\rangle\langle B\rangle\langle C\rangle, \tag{B5}$$

$$I_{31} = \langle ABC\rangle\langle D\rangle + \langle ABD\rangle\langle C\rangle + \langle ACD\rangle\langle B\rangle + \langle BCD\rangle\langle A\rangle, \tag{B6}$$

$$I_{22} = \langle AB\rangle\langle CD\rangle + \langle AC\rangle\langle BD\rangle + \langle AD\rangle\langle BC\rangle, \tag{B7}$$

$$I_{211} = \langle AB\rangle\langle C\rangle\langle D\rangle + \langle AC\rangle\langle B\rangle\langle D\rangle + \langle AD\rangle\langle B\rangle\langle C\rangle + \langle BC\rangle\langle A\rangle\langle D\rangle + \langle BD\rangle\langle A\rangle\langle C\rangle + \langle CD\rangle\langle A\rangle\langle B\rangle, \tag{B8}$$

$$I_{1111} = \langle A\rangle\langle B\rangle\langle C\rangle\langle D\rangle, \tag{B9}$$

$$I_{41} = \langle ABCD\rangle\langle E\rangle + \langle ABCE\rangle\langle D\rangle + \langle ABDE\rangle\langle C\rangle + \langle ACDE\rangle\langle B\rangle + \langle BCDE\rangle\langle A\rangle, \tag{B10}$$

$$I_{32} = \langle ABC\rangle\langle DE\rangle + \langle ABD\rangle\langle CE\rangle + \langle ABE\rangle\langle CD\rangle + \langle ACD\rangle\langle BE\rangle + \langle ACE\rangle\langle BD\rangle + \langle ADE\rangle\langle BC\rangle + \langle BCD\rangle\langle AE\rangle + \langle BCE\rangle\langle AD\rangle + \langle BDE\rangle\langle AC\rangle + \langle CDE\rangle\langle AB\rangle, \tag{B11}$$

$$I_{311} = \langle ABC\rangle\langle D\rangle\langle E\rangle + \langle ABD\rangle\langle C\rangle\langle E\rangle + \langle ABE\rangle\langle C\rangle\langle D\rangle + \langle ACD\rangle\langle B\rangle\langle E\rangle + \langle ACE\rangle\langle B\rangle\langle D\rangle + \langle ADE\rangle\langle B\rangle\langle C\rangle + \langle BCD\rangle\langle A\rangle\langle E\rangle + \langle BCE\rangle\langle A\rangle\langle D\rangle + \langle BDE\rangle\langle A\rangle\langle C\rangle + \langle CDE\rangle\langle A\rangle\langle B\rangle, \tag{B12}$$

$$I_{221} = \langle AB\rangle\langle CD\rangle\langle E\rangle + \langle AB\rangle\langle CE\rangle\langle D\rangle + \langle AB\rangle\langle DE\rangle\langle C\rangle + \langle AC\rangle\langle BD\rangle\langle E\rangle + \langle AC\rangle\langle BE\rangle\langle D\rangle + \langle AC\rangle\langle DE\rangle\langle B\rangle + \langle AD\rangle\langle BC\rangle\langle E\rangle + \langle AD\rangle\langle BE\rangle\langle C\rangle + \langle AD\rangle\langle CE\rangle\langle B\rangle + \langle AE\rangle\langle BC\rangle\langle D\rangle + \langle AE\rangle\langle BD\rangle\langle C\rangle + \langle AE\rangle\langle CD\rangle\langle B\rangle + \langle BC\rangle\langle DE\rangle\langle A\rangle + \langle BD\rangle\langle CE\rangle\langle A\rangle + \langle BE\rangle\langle CD\rangle\langle A\rangle, \tag{B13}$$

$$I_{2111} = \langle AB\rangle\langle C\rangle\langle D\rangle\langle E\rangle + \langle AC\rangle\langle B\rangle\langle D\rangle\langle E\rangle + \langle AD\rangle\langle B\rangle\langle C\rangle\langle E\rangle + \langle AE\rangle\langle B\rangle\langle C\rangle\langle D\rangle + \langle BC\rangle\langle A\rangle\langle D\rangle\langle E\rangle + \langle BD\rangle\langle A\rangle\langle C\rangle\langle E\rangle + \langle BE\rangle\langle A\rangle\langle C\rangle\langle D\rangle + \langle CD\rangle\langle A\rangle\langle B\rangle\langle E\rangle + \langle CE\rangle\langle A\rangle\langle B\rangle\langle D\rangle + \langle DE\rangle\langle A\rangle\langle B\rangle\langle C\rangle, \tag{B14}$$

$$I_{11111} = \langle A\rangle\langle B\rangle\langle C\rangle\langle D\rangle\langle E\rangle. \tag{B15}$$

These equations have been derived for the expectation values of operators. However, they also work for averages of phase space variables. If the first-order averages are all zero, Eqs. (B1)–(B3) can be simplified as follows:

$$\langle ABC\rangle \approx 0, \tag{B16}$$

$$\langle ABCD\rangle \approx I_{22}, \tag{B17}$$

$$\langle ABCDE\rangle \approx I_{32}. \tag{B18}$$

On the basis of Eqs. (B11) and (B16), we have $I_{32} \approx 0$ and thus Eq. (B18) becomes

$$\langle ABCDE\rangle \approx 0. \tag{B19}$$

Thereby, third- and fifth-order averages are all zero when first-order averages are zero.

[1]G. C. Sosso, J. Chen, S. J. Cox, M. Fitzner, P. Pedevilla, A. Zen, and A. Michaelides, Chem. Rev. **116**, 7078 (2016).
[2]J. A. Lemkul, J. Huang, B. Roux, and A. D. MacKerell, Jr., Chem. Rev. **116**, 4983 (2016).
[3]J. L. Klepeis, K. Lindorff-Larsen, R. O. Dror, and D. E. Shaw, Curr. Opin. Struct. Biol. **19**, 120 (2009).
[4]L. J. Wang, Q. K. Li, Z. Shuai, L. P. Chen, and Q. Shi, Phys. Chem. Chem. Phys. **12**, 3309 (2010).
[5]D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).
[6]R. Kosloff, Annu. Rev. Phys. Chem. **45**, 145 (1994).
[7]H.-D. Meyer and G. A. Worth, Theor. Chem. Acc. **109**, 251 (2003).
[8]N. Makri, Annu. Rev. Phys. Chem. **50**, 167 (1999).
[9]S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, Annu. Rev. Phys. Chem. **64**, 387 (2013).
[10]O. V. Prezhdo, Theor. Chem. Acc. **116**, 206 (2006).
[11]M. Thoss and H. B. Wang, Annu. Rev. Phys. Chem. **55**, 299 (2004).
[12]R. Kapral, Annu. Rev. Phys. Chem. **57**, 129 (2006).
[13]M. K. Lee, P. F. Huo, and D. F. Coker, Annu. Rev. Phys. Chem. **67**, 639 (2016).
[14]B. F. E. Curchod and T. J. Martínez, Chem. Rev. **118**, 3305 (2018).
[15]J. C. Tully, J. Chem. Phys. **137**, 22A301 (2012).
[16]L. J. Wang, O. V. Prezhdo, and D. Beljonne, Phys. Chem. Chem. Phys. **17**, 12395 (2015).
[17]L. J. Wang, A. Akimov, and O. V. Prezhdo, J. Phys. Chem. Lett. **7**, 2100 (2016).
[18]J. E. Subotnik, A. Jain, B. Landry, A. Petit, W. J. Ouyang, and N. Bellonzi, Annu. Rev. Phys. Chem. **67**, 387 (2016).
[19]R. Crespo-Otero and M. Barbatti, Chem. Rev. **118**, 7026 (2018).
[20]A. V. Akimov and O. V. Prezhdo, Chem. Rev. **115**, 5797 (2015).
[21]O. V. Prezhdo and Yu. V. Pereverzev, J. Chem. Phys. **113**, 6557 (2000).
[22]H. Miyachi, Y. Shigeta, and K. Hirao, Chem. Phys. Lett. **432**, 585 (2006).
[23]E. Pahl and O. V. Prezhdo, J. Chem. Phys. **116**, 8704 (2002).
[24]C. Brooksby and O. V. Prezhdo, Chem. Phys. Lett. **378**, 533 (2003).
[25]O. V. Prezhdo and Y. V. Pereverzev, J. Chem. Phys. **116**, 4450 (2002).
[26]K. Igumenshchev and O. V. Prezhdo, Phys. Rev. E **84**, 026616 (2011).
[27]D. S. Kilin, O. V. Prezhdo, and M. Schreiber, J. Phys. Chem. A **111**, 10212 (2007).
[28]D. S. Kilin, Yu. V. Pereversev, and O. V. Prezhdo, J. Chem. Phys. **120**, 11209 (2004).
[29]L. J. Wang, A. V. Akimov, L. P. Chen, and O. V. Prezhdo, J. Chem. Phys. **139**, 174109 (2013).
[30]C. Brooksby and O. V. Prezhdo, Chem. Phys. Lett. **346**, 463 (2001).
[31]J. M. Kumpula, A. P. Sutton, and K. Kaski, Chem. Phys. **324**, 659 (2006).
[32]Y. Shigeta, H. Miyachi, and K. Hirao, J. Chem. Phys. **125**, 244102 (2006).
[33]Y. Shigeta, H. Miyachi, and K. Hirao, Chem. Phys. Lett. **443**, 414 (2007).
[34]Yu. V. Pereverzev, A. Pereverzev, Y. Shigeta, and O. V. Prezhdo, J. Chem. Phys. **129**, 144104 (2008).
[35]Y. Shigeta, J. Chem. Phys. **128**, 161103 (2008).
[36]Y. Shigeta, R. Harada, M. Kayanuma, and M. Shoji, Int. J. Quantum Chem. **115**, 300 (2015).
[37]Y. Shigeta, Chem. Phys. Lett. **461**, 310 (2008).
[38]Y. Shigeta, T. Inui, T. Baba, K. Okuno, H. Kuwabara, R. Kishi, and M. Nakano, Int. J. Quantum Chem. **113**, 348 (2013).
[39]B. Smith and A. V. Akimov, J. Chem. Phys. **148**, 144106 (2018).
[40]V. I. Tatarski, Sov. Phys. Usp. **26**, 311 (1983).
[41]O. V. Prezhdo, J. Chem. Phys. **117**, 2995 (2002).
[42]E. Heatwole and O. V. Prezhdo, J. Chem. Phys. **126**, 204108 (2007).
[43]E. Heatwole and O. V. Prezhdo, J. Chem. Phys. **121**, 10967 (2004).
[44]E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[45]J. Ono and K. Ando, J. Chem. Phys. **137**, 174503 (2012).
[46]T. Ohsawa and M. Leok, J. Phys. A: Math. Theor. **46**, 405201 (2013).
[47]H. Weyl, Z. Phys. **46**, 1 (1927).
[48]E. Wigner, Phys. Rev. **40**, 749 (1932).
[49]H. J. Groenewold, Physica **12**, 405 (1946).
[50]J. E. Moyal, Math. Proc. Cambridge Philos. Soc. **45**, 99 (1949).
[51]A. V. Akimov and O. V. Prezhdo, J. Chem. Phys. **137**, 224115 (2012).
[52]D. E. Manolopoulos, J. Chem. Phys. **117**, 9552 (2002).
[53]K. Toukan and A. Rahman, Phys. Rev. B **31**, 2643 (1985).
[54]A. Donoso and C. C. Martens, Phys. Rev. Lett. **87**, 223202 (2001).