Global Representation of Maslov-Type Semiclassical Wave Function and Its Spectrum in a Small Number of Classical Trajectories

Kazuo Takatsuka and Atsuko Inoue

Graduate School of Human Informatics, Nagoya University, Nagoya 464-01, Japan
(Received 27 June 1996)

An explicit solution to the Maslov-type semiclassical theory for propagating a wave function, rather than evolving in time the Feynman kernel, is presented. It turns out that the present solution bears distinguished advantages over the semiclassical kernel, one of the most remarkable examples of which is the far less number of classical trajectories required for the propagation, basically proportional to $P^{2N} \sim P^{3N}$ for the kernel while only to P^N in our solution, where N is the dimension in configuration space and P is the number of sampling points in each dimension. As an illustrative example to show the validity of the solution, the theory is applied to the calculation of eigenvalues of the Morse oscillators, giving accurate results in a compact way.   [S0031-9007(97)02397-1]

Semiclassical mechanics has long been a fundamental theory to investigate the quantum effect on the dynamics of many-body systems. 1994 was a year when the studies of the primitive semiclassical approximation to the Feynman path integrals [1,2] have been settled into the final stage due to the outstanding works by Kay [3], Sepulveda and Heller [4], and Brumer and his co-workers [5]. (By the primitive semiclassical approximation, we mean the level of approximation equivalent to the lowest-order stationary-phase approximation [2].) This progress was triggered by an important contribution due to Heller [6], and has been pushed in part by the general interests in the so-called quantum chaos [5(b),7]. There can be various representations for the semiclassical kernel, the typical one being [3,4]

$$K(q, q_0) = (4\pi^2 i \hbar^2)^{-\frac{N}{2}} \int dp_0 \left| \frac{\partial p_t}{\partial p_0} \right|^{\frac{1}{2}}$$
$$\times \exp\left[\frac{i}{\hbar} S(q_t, q_0, t) \right.$$
$$\left. - i\frac{\pi \mu}{2} + \frac{i}{\hbar} p_t \cdot (q - q_t) \right], \quad (1)$$

where, among the other obvious notations, (q_t, p_t) is the end point at time t of a classical trajectory starting from (q_0, p_0) in phase space. q is an independent variable in the N-dimensional configuration space, and μ is the Maslov index [1,2,5(a)]. The significant improvements achieved by expressions of this kind are (i) the trajectories used in the kernel are specified by the initial points (q_0, p_0) (release from the double-ended boundary problem) and (ii) the amplitude factor $|\partial p_t / \partial p_0|^{1/2}$ does not diverge at caustics. These characteristics are common to those of the so-called phase-space path integrals [8]. One big problem left behind though is large dimensionality in integration to calculate overlap integrals like a correlation function [cf. Eq. (9)] and the scattering (S) matrix that are generally defined as

$$\langle \Phi | \Psi(t) \rangle = \int dq\, dq_0 \Phi^*(q) K(q, q_0) \Psi(q_0, 0), \quad (2)$$

which is a $2N$-dimensional integral. Even $3N$-dimensional integration is charged if the form of Eq. (1) is employed. This burden still hinders the semiclassical theory from being applied to large systems.

In the present Letter we report an explicit solution to the multidimensional Maslov (primitive) semiclassical theory, which is for the propagation of wave functions rather than the Feynman kernel. (It is sometimes misunderstood that the semiclassical theories for the kernel and wave functions are the same under the common name of the WKB theory. But they are actually not, as seen below. To stress the difference, we term the semiclassical mechanics for wave functions the Bohm-Maslov theory, rather than the customarily used WKB theory.) In some aspects, the kernel is more general and flexible [2,7(c)]. However, one can find distinguished advantages in the Bohm-Maslov semiclassical solution. In particular, an emphasis in this Letter is placed on a possibility that this solution can be applied to much larger systems that cannot be handled with the semiclassical kernel.

The Bohm-Maslov semiclassical mechanics begins with the following wave function

$$\Psi(q, t) = F(q, t) \exp\left[\frac{i}{\hbar} S_{\mathrm{cl}} \right], \quad (3)$$

which is to be propagated in terms of the equations of motion of the lowest-order approximation in $\hbar$ to the Schrödinger equation. The higher order effects are taken into account in different ways by the Bohm and Maslov theories: the so-called quantum potential is considered in the Bohm theory [9], while Maslov takes into account the hierarchical series of the quantum transport [10]. We will show our own way of how to treat the higher effects [11]. S_{cl} is the classical action that satisfies the Hamilton-Jacobi equation. Note that picking up an S_{cl} among the various possible forms is equivalent to specifying an initial condition that is imposed on the classical trajectories [12]. For

later convenience, we choose S_{cl} to be the F_2-type generating function [12] such that $S_{cl}(q, p_0, t) = F_2(q, p_0, t) = F_1(q, q_0, t) + q_0 p_0$. [$F_1$ and F_2 should not be confused with $F(q, t)$ of Eq. (3).]

The function $F(q, t)$ is determined by the following equation of motion [10]

$$\frac{\partial F}{\partial t} + \nu \cdot \nabla F = -\frac{1}{2}(\nabla \cdot \nu)F, \qquad (4)$$

where $\nu = \frac{\partial S_{cl}}{\partial q}$ is the classical velocity. We use the mass-weighted coordinates throughout so that all the masses are scaled to unity. Equation (4) tells us to integrate its right-hand side along a classical trajectory, which will give rise to an exponential form like $F(q(t)) = F(q(0)) \exp(-\frac{1}{2} \int_0^t dt \nabla \cdot \nu)$. But, this formal solution turns out to break down at caustics.

An alternative way can start from the following observation:

$$\frac{\partial F^2}{\partial t} + \nabla \cdot (\nu F^2) = 0. \qquad (5)$$

Note that F^2 rather than $|F|^2$ is considered in this "equation of continuity" (notice that F^2 can be negative). F^2 can be readily integrated locally along a classical path in terms of a Jacobian determinant $\partial q_t / \partial q_0$ which is a minor determinant of the so-called stability matrix [2,7,8,12]. $(\partial q_t / \partial q_0)^{-1} = \partial^2 S_{cl}(q_t, p_0, t)/(\partial q_t \partial p_0)$ is interpreted as the density of families of classical trajectories which are labeled with their initial configuration coordinates q_0. It is not difficult to derive from the Hamilton-Jacobi equation for $S_{cl}(q_t, p_0, t)$ that

$$\frac{\partial}{\partial t}\left(\frac{\partial q_t}{\partial q_0}\right)^{-1} + \nabla \cdot \left[\nu\left(\frac{\partial q_t}{\partial q_0}\right)^{-1}\right] = 0. \qquad (6)$$

Furthermore, one has the initial condition $(\partial q_t / \partial q_0)^{-1} = 1$, since $q_t = q_0$ at $t = 0$. Thus $(\partial q_t / \partial q_0)^{-1}$ can be regarded as the local representation of the Green function of Eq. (5). On comparing Eqs. (5) and (6), together with the initial condition above, one immediately has

$$F(q_t, t) = F(q_0, 0)\left(\frac{\partial q_t}{\partial q_0}\right)^{-\frac{1}{2}} = F(q_0, 0)\left|\frac{\partial q_t}{\partial q_0}\right|^{-\frac{1}{2}}$$
$$\times \exp\left[\frac{i\pi M}{2}\right], \qquad (7)$$

where the derivative $\partial q_t / \partial q_0$ is taken under the fixed initial momentum p_0, and M is the Maslov index in this representation that counts the number of zeros of $\partial q_t / \partial q_0$ up to the degeneracy. Thus the local solution, denoted by $\Psi_{local}^{p_0}(q_t, t)$, has been obtained, which is to be propagated along a trajectory that is generated by $S_{cl}(q, p_0, t)$ with the fixed initial momentum p_0.

The global wave function composed of the local solutions is then written as

$$\Psi_{p_0}(q, t) = \int \delta(q - q_t)\Psi_{local}^{p_0}(q_t, t)dq_t$$
$$= \int \delta(q - q_t)\Psi_{local}^{p_0}(q_t, t)\left|\frac{\partial q_t}{\partial q_0}\right|dq_0$$
$$= \int \delta(q - q_t(q_0, p_0))F(q_0, 0)\left|\frac{\partial q_t}{\partial q_0}\right|^{\frac{1}{2}}$$
$$\times \exp\left[\frac{i}{\hbar}S_{cl}(q_t, p_0, t) + \frac{i\pi M}{2}\right]dq_0. \qquad (8)$$

This expression is the final form of our primitive semiclassical wave function. The local solution $F(q_t, t)$ in Eq. (7) diverges at every caustic point, at which the Jacobian determinant $\partial q_t / \partial q_0$ becomes zero. On the other hand, the global solution Eq. (8) does not have the divergence due to the transformation of the integral variable from q_t to q_0. The mathematical mechanism for the divergence to disappear is essentially the same as those for the semiclassical kernel like [3–6].

The form of Eq. (8) brings about a conceptual progress in the study of quantum-classical correspondence [11]. In the present Letter, however, we stress only the simplicity and tractability of the theory. Suppose we want to calculate a molecular spectrum in terms of the autocorrelation function $C(t)$, which is represented as

$$C(t) = \langle\Psi_{p_0}(0)|\Psi_{p_0}(t)\rangle$$
$$= \int F^*(q_t, 0)F(q_0, 0)\left|\frac{\partial q_t}{\partial q_0}\right|^{\frac{1}{2}}$$
$$\times \exp\left[-\frac{i}{\hbar}p_0 q_t + \frac{i}{\hbar}S_{cl}(q_t, p_0, t) + \frac{i\pi M}{2}\right]dq_0. \qquad (9)$$

The Fourier transform, the Fast Fourier Transform (FFT) in practice, is applied to $C(t)$ to yield the energy spectra. Because of the presence of the delta function in Eq. (8), $C(t)$ in Eq. (9) still remains to be an N-dimensional integral in q_0 coordinates. This remarkable advantage should be compared with Eq. (2), which is a $2N$- or $3N$-dimensional integral. (The physical reason why the difference could happen will be explained in a greater detail in our full publication [11].) This difference in the dimensionality becomes tremendous in practice when N is as large as, say, ten, which is still not very large for molecular applications.

The drastic simplification above arises at the sacrifice that the Bohm-Maslov wave packet approach is more restrictive than the kernel: The kernel should be general enough to be capable of propagating any initial wave function, and has many theoretical advantages common to the other general Green functions [2]. On the other hand, the initial wave function of our solution is limited to the form of Eq. (3) and characterized by a momentum vector p_0. The price for this simplification is therefore that if one is interested in propagating a general wave function,

an elaboration of expansion in $\Psi_{p_0}(q,0)$ is necessary. (Note that this expansion should not be confused with the Fourier transform, even if $\Psi_{p_0}(q,0)$ is characterized with the momentum. $\Psi_{p_0}(q,0)$ is a square-integrable wave function and thus the continuous parameterization in p_0 is not always necessary for the practical expansion [11].) The point, nevertheless, is that some of the physical observables can be calculated even if the initial wave packet is limited to the form of Eq. (3), as will be verified below.

In order to show the validity and efficiency of the expressions of Eqs. (8) and (9), we apply to the one-dimensional Morse problem, namely,

$$H = \frac{p^2}{2} + D[1 - \exp(-\lambda x)]^2, \qquad (10)$$

for which the analytical expression of energy is known. The parameters used are $D = 5000$, $\lambda = 0.01$ and $D = 40$, $\lambda = 0.1$. The initial function $F(q,0)$ is arbitrarily selected to be Gaussian centered at q_c such that

$$\Psi(q,0) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp[-\alpha(q - q_c)^2] \exp\left(\frac{i}{\hbar} p_0 q\right), \quad (11)$$

which is simply a coherent-state wave packet [2,9]. The Gaussian is deformed into a non-Gaussian form eventually with the propagation of Eq. (8), if the potential is not quadratic. Incidentally, Heller has constructed an interesting semiclassical theory in which the Gaussian form like Eq. (11) is retained with its center, the associated momentum, and the exponent (α) being determined simultaneously on a "locally" quadratic potential [13]. The parameters in Eq. (11) are set to $\alpha = 6.0$, $q_c = 2.0$, $p_0 = 0.0$, and $\hbar = 1$. The numerical integration over q_0 has been carried out with the Gauss-Legendre quadrature [14]. In other words, the initial conditions $(q_{0i}, p_0) = (q_{0i}, 0.0)$ $(i = 1, \ldots, N_p)$ for running the trajectories are automatically selected by the quadrature points. Note again that the path-integral formalisms [3–6,8] generally require the number of trajectories to the order of N_p^2 (or N_p^3 if the additional integration as in [3–5,8] is taken into account), which should result in a dramatic difference in a large system. (Note that writing down the semiclassical expressions like Eqs. (8) and (9) should be distinguished from the practical method of numerical integration. For instance, although we have used the Gaussian quadrature here, the cellular dynamics of Heller [6] could be applied to our integral as well to reduce the number of the required trajectories.)

The numerical comparison with the exact values are made in Table I. The number of trajectories N_p is only 20 and 30 for the upper and lower lists, respectively, in Table I. The resolution of the energy, namely, the distance of the neighboring grid points in the energy domain determined by the present FFT calculation, is 0.030 67. However, the energies beyond that limit can be estimated with a simple method proposed by one

TABLE I. The semiclassical eigenvalues for the Morse oscillator.

Quantum Number	Exact	Semiclassical
$D = 5000$[a]	$\lambda = 0.01$[a]	(1.960^{b})
0	0.499 99	0.50221 [c,d]
1	1.499 89	1.50008
2	2.499 69	2.49862
3	3.499 39	3.49926
4	4.498 99	4.49903
5	5.498 49	5.49877
6	6.497 89	6.49709
7	7.497 19	7.49773
8	8.496 39	8.49750
9	9.495 48	9.49749
10	10.494 49	10.49501
$D = 40$[a]	$\lambda = 0.1$[a]	(1.314^{b})
0	0.44596	0.45889 [c,e]
1	1.33039	1.34003
2	2.20482	2.20461
3	3.06925	3.07012
4	3.92367	3.90961
5	4.76810	4.75605

[a]The parameters in the Morse function, Eq. (10).
[b]The potential energy at the center of the initial Gaussian wave packet.
[c]The resolution limit of the FFT in this calculation is 0.030 67.
[d]$N_p = 20$.
[e]$N_p = 30$.

of the present authors, in which the so-called window technique is not used [15]. The numbers in the entry of the semiclassical theory in Table I have been obtained in this way. It is clear that our semiclassical results are very accurate. Extremely accurate calculations to converge to the semiclassical limit may require a larger number of trajectories, but N_p here (20 and 30) are the numbers at which the results begin to converge. (The convergence was checked by looking at the correlation functions.) Also, a long-time evolution of the correlation function on an anharmonic potential tends to need more trajectories, since the distribution of the trajectories in space becomes wider as the time passes. We have carried out other higher dimensional calculations and obtained the similar accuracy, and thus it has been verified that the method is highly promising.

Moreover, it is quite obvious that our calculation has been very compact. As an example, we are reminded of the recent work by Kinugawa [16], where he used as many trajectories as the order of 10^4 to 10^5 for Monte Carlo sampling from phase space for $N = 1$ to evaluate the Morse spectra using Heller's version of the semiclassical kernel [6]. Although a comparison in terms of the number of trajectories alone does not necessarily make good sense, it is clear that Eqs. (8) and (9) can

be utilized to investigate the quantum (semiclassical) effects in large systems that could not be done before. The actual applications to high dimensional systems including the propagation of a wave function in a chaotic situation and other theoretical analyses such as the higher approximation than the primitive semiclassical theory will be reported in our future publication [11].

[1] (a) M. V. Berry and K. E. Mount, Rep. Prog. Phys. **35**, 315 (1972); (b) M. S. Child, *Semiclassical Mechanics with Molecular Approximations* (Clarendon Press, Oxford, 1991).

[2] L. S. Schulman, *Technique and Applications of Path Integration* (John Wiley & Sons, Inc., New York, 1981).

[3] K. G. Kay, J. Chem. Phys. **100**, 4432 (1994).

[4] M. A. Sepulveda and E. J. Heller, J. Chem. Phys. **101**, 8004 (1994).

[5] (a) G. Campolieiti and P. Brumer, Phys. Rev. A **50**, 997 (1994); (b) D. Provost and P. Brumer, Phys. Rev. Lett. **74**, 250 (1995).

[6] E. J. Heller, J. Chem. Phys. **94**, 2723 (1991).

[7] (a) A. M. Ozorio de Almeida, *Hamiltonian Systems: Chaos and Quantization* (Cambridge Univ. Press, Cambridge, 1988); (b) M. Tabor, *Chaos and Integrability in Nonlinear Dynamics* (Wiley, New York, 1989); (c) M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer, New York, 1990); (d) L. E. Reidel, *The Transition to Chaos* (Springer-Verlag, Berlin, 1992); (e) K. Nakamura, *Quantum Chaos* (Cambridge University Press, Cambridge, 1993).

[8] K. Takatsuka, Phys. Rev. Lett. **61**, 503–506 (1988); K. Takatsuka, Phys. Rev. A **39**, 5961–5973 (1989); K. Takatsuka, Phys. Rev. A **45**, 4326–4339 (1992).

[9] A. Messiah, *Quantum Mechanics* (John Wiley, New York, 1960).

[10] V. P. Maslov and M. V. Feodoriuk, *Semi-Classical Approximation in Quantum Mechanics* (Reidel, Dordrecht, 1981).

[11] A. Inoue and K. Takatsuka (to be published).

[12] H. Goldstein, *Classical Mechanics* (Addison-Wesley, New York, 1980).

[13] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975); E. J. Heller, J. Chem. Phys. **65**, 4979 (1976).

[14] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).

[15] K. Takatsuka, J. Comput. Phys. **102**, 374 (1992).

[16] T. Kinugawa, Chem. Phys. Lett. **235**, 395 (1995).