Globally Uniform Semiclassical Expressions for Time-Independent Wave Functions

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A semiclassical approximation is presented which describes the time-independent wave function as an integral over the Lagrangian manifold associated with the state. The function produced is free of caustic singularities and satisfies the Schrödinger equation with an error that vanishes everywhere uniformly in the classical limit. Illustrative calculations are presented for one-dimensional systems.

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Semiclassical approximations for time-independent wave functions have found many applications in physics and chemistry [1–3]. Unfortunately, the simplest (primitive or WKB) semiclassical expressions have infinite singularities at caustics. At such boundaries between classically allowed and forbidden regions of space, the semiclassical approximation breaks down the expressions become incorrect. Although it is possible, in principle, to remedy this problem by smoothly piecing together semiclassical expressions that are locally valid in different regions of space [4], this requires switching back and forth between different mixed coordinate-momenta representations and becomes tedious for multidimensional systems [5].

It is clear that simple, globally uniform semiclassical expressions for the wave function are highly desirable. Ideally, these should consist of single, explicit formulas that are accurate over all space and that become uniformly exact everywhere in the classical limit. Unfortunately, the conventional approaches to developing uniform approximations become complicated for multidimensional systems and the resulting applications can be difficult, even when the approximations are not global [2,6]. Indeed, it is only in the one-dimensional case that the usual treatments have yielded practical, globally uniform, expressions for wave functions of bound systems [7].

In this paper we obtain globally uniform semiclassical expressions for time-independent wave functions of systems having arbitrary dimension. The formulas apply to states in the regular part of phase space in cases where tunneling from one classically allowed region to another is unimportant. The expressions allow simple evaluation of wave functions without switching between multiple representations or matching functions at boundaries. We verify the semiclassical formulas by performing numerical tests for one-dimensional systems; calculations for multidimensional systems will be presented elsewhere.

To simplify our presentation, we initially consider a one-dimensional system. Our uniform semiclassical expression for the wave function is then given by

$$\psi(x) = N \int C_t \exp\left(-\left[\gamma_t (x - q_t)^2 + i p_t (x - q_t) + i \int_0^t p_\tau \dot{q}_\tau \, d\tau \right] \Big/ \hbar \right) dt , \quad (1)$$

where p_t and q_t are the momentum and coordinate at time t for the classical trajectory which corresponds to quantum state $|\psi\rangle$ according to the usual WKB prescription. The preexponential factor is defined by

$$C_t = (\dot{p}_t - 2i\gamma_t \dot{q}_t)^{1/2}, \quad (2)$$

with the phase of the square root chosen to make C_t a continuous function of t. The time integration is over the period of motion $(0, T)$ for a bound system and over an infinite interval otherwise. In the simplest case, γ is an arbitrary, finite, positive constant. More generally, it may be chosen as an arbitrary, complex, analytic function of t satisfying $\mathrm{Re}\gamma > 0$ and $|\gamma| < \infty$. For a bound system, γ must, additionally, be periodic with period T. Finally, N is a normalization constant.

We wish to verify that Eq. (1) is a uniform asymptotic solution to the Schrödinger equation. Since the details of the demonstration closely parallel those presented in Appendix D of [8], we will only summarize the main steps here. Our strategy is to examine the effect of applying $\hat{H} - E$ to the wave function, where $\hat{H}$ is the Hamiltonian operator and E is the classical energy associated with (p_t, q_t). The result of this operation would be identically zero for all x if ψ were the exact wave function at energy E. More generally, it is a function that measures the error in $\psi(x)$. To demonstrate that our expression is a uniform asymptotic approximation, we show that this error is proportional to $\hbar^2$ and is bounded for all (finite) values of the coordinate.

To accomplish this, we let $\hat{H} - E$ act on the integrand and expand the result in powers of $x - q_t$. The product of $(x - q_t)^n$ and the exponential factor can then be expressed in terms of time-derivative operators acting on the exponential factor. We reverse the direction of these derivatives by integrating by parts an appropriate number

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of times. Contributions from the integration limits vanish because the integrands are periodic (for bound systems) or because they tend to zero at the limits for any finite x (for unbound systems).

The resulting integral then consists of terms proportional to $\hbar^n$, $n = 0, 1, 2, \ldots$. Terms of zeroth and first order in $\hbar$ vanish as a result of the classical equations of motion and Eq. (2) for C_t. The only problematic factors in the remaining, higher order, terms of the integrand are quantities of the form $z_{lm} = \gamma^l(\dot{p}_t - 2i\gamma_t\dot{q}_t)^{-m/2}$, where $l = 0, 1, 2$, and m takes on various integer values. Such functions would cause the integrand to become infinite if they diverged for some real value of t. However, since $\dot{p}_t$ and $\dot{q}_t$ do not vanish simultaneously (except at a fixed point in phase space), the z_{lm} never diverge along a real trajectory if γ is restricted as described above. Under these circumstances, the integrand is bounded for all t and the integral is itself bounded for all values of x, thus establishing the desired result.

Applying similar methods, it is possible to verify the following expression for the wave function in the case of a system with f degrees of freedom:

$$\psi(\mathbf{x}) = N \int d\theta\, C_\theta \times \exp\left(\left[-(\mathbf{x} - \mathbf{q}_\theta)\cdot\gamma_\theta\cdot(\mathbf{x} - \mathbf{q}_\theta) + i\mathbf{p}_\theta\cdot(\mathbf{x} - \mathbf{q}_\theta) + i\int^\theta \mathbf{p}\cdot(\partial\mathbf{q}/\partial\theta')\,d\theta'\right] \Big/ \hbar\right), \quad (3)$$

where the integral is over the Lagrangian manifold associated with the state and θ is a vector containing f coordinates which span the manifold. $\mathbf{p}$ and $\mathbf{q}$ are f-dimensional vectors containing the system's momenta and coordinates. γ is an f-dimensional square matrix whose elements may be finite constants or, more generally, arbitrary, complex, analytic functions of θ. However, the real parts of all eigenvalues of this matrix must be positive and, for bound systems, the elements of γ must be 2π periodic in each of the angle variables. The action integral is along an arbitrary path on the manifold originating from an arbitrary constant point. The preexponential factor is given by

$$C_\theta = [\det(\partial\mathbf{p}/\partial\theta - 2i\gamma\partial\mathbf{q}/\partial\theta)]^{1/2}, \quad (4)$$

where the partial derivatives represent square matrices defined by

$$(\partial\mathbf{z}/\partial\theta)_{ij} = \partial z_i/\partial\theta_j, \qquad z = p, q, \quad (5)$$

and where the phase of the square root is chosen to make C_θ a continuous function of θ along the path used to evaluate the action integral.

It is now straightforward to verify the following properties of the one-dimensional expression (with analogous remarks applying to the general result): (1) With appropriate choices of γ, it is an exact representation of $\psi(x)$ [9] for systems with Hamiltonians that are at most quadratic functions of the momenta and coordinates. (2) It reduces to the primitive WKB expression when the stationary phase approximation is applied to the integral. (3) It also goes over to the WKB expression in the limit as $\gamma \to \infty$. (4) It reduces to the Fourier transform of the primitive WKB wave function in the momentum representation in the limit as $\gamma \to 0$.

We note that the wave functions obtained in the last two limiting cases are not uniform approximations since γ does not obey the stated restrictions which imply that it must not be chosen to be either ∞ or 0. The $\gamma = \infty$ wave function breaks down at caustics where $\dot{x}_t$ vanishes while the $\gamma = 0$ result breaks down more globally due to singularities in the momentum wave function where $\dot{p}_t$ vanishes. The Maslov [4] procedure for producing a globally uniform result would be to multiply the primitive wave functions by switching functions which essentially kill the singularities, apply the modified $\gamma = \infty$ and $\gamma = 0$ expressions in their respective regions of validity, and smoothly join the results together. Our single expression with an intermediate choice for γ, however, remains valid everywhere and can be used for all values of x without having to introduce switching functions, shuttle between representations, or match wave functions. In effect, the expression interpolates between the coordinate and momentum representations and thereby avoids the caustics which limit the useful domain of each of these representations.

The form of Eqs. (1) and (3) clearly suggests a relationship to earlier semiclassical treatments associated with coherent states. Indeed, our results can be regarded as time-independent analogs of certain coherent-state–based uniform expressions for the time-dependent propagator [8,10,11]. In addition, for choices of γ as particular complex θ-dependent functions, Eq. (3) reduces to expressions for the time-independent wave function previously obtained by Littlejohn [12]. A more distant family tie exists between our results and a number of other coherent state treatments of the time-independent wave function [13].

In the case where γ is chosen to be constant and real, our results are closely related to those of the frozen Gaussian approximation (FGA) of Heller and co-workers [9,14]. This popular semiclassical treatment was derived [9] by heuristically generalizing an expression for wave functions of systems with quadratic potentials. The FGA expression is the same form as ours except that it replaces the coefficient C_t with a factor that can be written as $B_t e^{-i\boldsymbol{\alpha}\cdot\boldsymbol{\omega}t/4}$, where B_t is a positive function of t and $\boldsymbol{\alpha}$ and $\boldsymbol{\omega}$ are vectors containing the Maslov indices and frequencies for the various degrees of freedom. In the one-dimensional case, it turns out that $B_t = |C_t|$ so that the two treatments differ only in the phase of the prefactor. In systems with more than one degree of freedom, however, B_t is not directly related to C_t even for separable Hamiltonians, so that the two approximations differ more strongly.

We now describe calculations which compare the results of our approximation, for the case of real constant γ, to the results of accurate quantum treatments and of the FGA. We examine two one-dimensional, anharmonic systems. The first system is a quartic oscillator with the Hamiltonian

$$\hat{H} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + c_1 x^2 + c_2 x^4, \tag{6}$$

where $c_1 = 0.5$ and $c_2 = 0.1$. The quantum calculation was carried out by diagonalizing $\hat{H}$ in a large harmonic oscillator basis. In the uniform semiclassical calculations, the trajectories associated with various quantum states were determined by numerically searching for orbits satisfying the Bohr quantization condition. The integration over t in Eq. (1) was performed by the trapezoid rule, and N was determined numerically to normalize the wave function to unity. The FGA calculation differed from above only in the replacement of C_t by $|C_t|e^{-i\omega t/2}$ (where $\omega = 2\pi/T$ is the classical frequency of motion at the energy of interest) and in the value of γ used. For the case of the FGA, the choice $\gamma = \omega/2$ was found to yield nearly optimal accuracy and was used in the calculations. For the uniform treatment, the choice $\gamma = \omega/2$ ($n = 0$) and $\gamma = \omega$ ($n > 0$) was found to be more accurate and was consequently applied [15]. It should be mentioned that the wave functions produced in both calculations are rather insensitive to γ and moderate variations in our choices do not change the qualitative results presented here.

As a measure of the errors in the semiclassical approximations, we examined the quantity $1 - \Omega$, where $\Omega = |\langle\psi|\psi^q\rangle|$ and ψ^q is the accurate quantum wave function. Figure 1 shows that both the uniform and FGA wave functions are in excellent agreement with the quantum functions for the full range of n investigated, but the uniform results are much more accurate than those of the FGA for $n > 0$. In fact, the uniform technique becomes monotonically more accurate with increasing n, as expected of a semiclassical approximation, while the FGA becomes progressively less accurate as n is increased. This can be understood by recalling that the validity of the FGA is based on the harmonic approximation for the potential which becomes less accurate as n increases.

The second system examined was the Morse oscillator described by the Hamiltonian

$$\hat{H} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + D(1 - e^{-\beta x})^2, \tag{7}$$

where $\beta = (2D)^{-1/2}$. For the value $D = 10.5$ used here, the potential supports 20 bound states. The calculations were performed in the same way as for the first system except that (a) quantum wave functions and semiclassical energies were obtained from analytical expressions, and (b) the values of γ that were found to be nearly optimal and that were used in the calculations were $\omega_0/2$ and $\omega/2$ for the FGA and uniform cases, respectively, where ω_0 is the harmonic frequency of motion for low energy vibrations.

It is clear from Fig. 2 that, for large n, the FGA is far less satisfactory for this system than it is for the quartic oscillator. Indeed, Fig. 3 shows that the high-energy FGA functions differ strongly from the quantum results near the turning points and are out of phase with the quantum and uniform functions. The latter effect, which is mostly responsible for the large error described in Fig. 2, is a direct consequence of the incorrect phase of the FGA integrand. The error is more pronounced for the Morse system than for the previous one due to the asymmetry of the present potential.

Although, for this system, the uniform approximation is much more accurate than the FGA for all n, this accuracy does not vary monotonically with n, as it did in the previous case. As n is raised, $1 - \Omega$ first decreases but then increases as one nears the dissociation limit ($E = D$); see Fig. 2. Figure 3 reveals that this is primarily due to small errors in the uniform approximation's description of the wave function in the region lying near and beyond the right turning point.

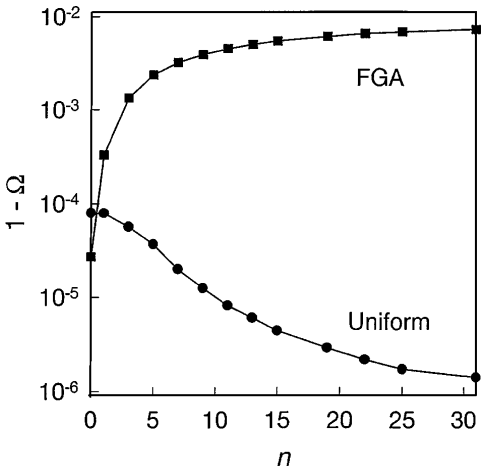

FIG. 1. Error in the uniform semiclassical and FGA wave functions vs quantum number for the quartic oscillator.

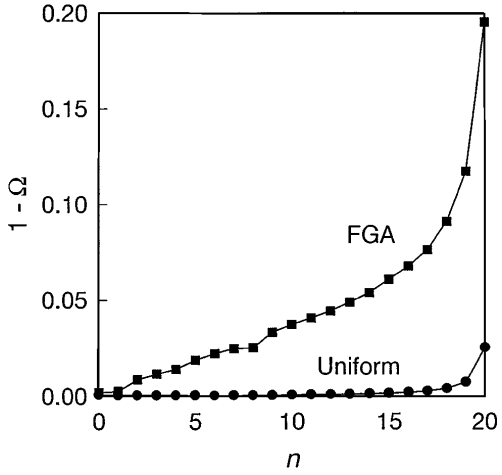

FIG. 2. Error in the uniform semiclassical and FGA wave functions quantum number for the Morse oscillator.

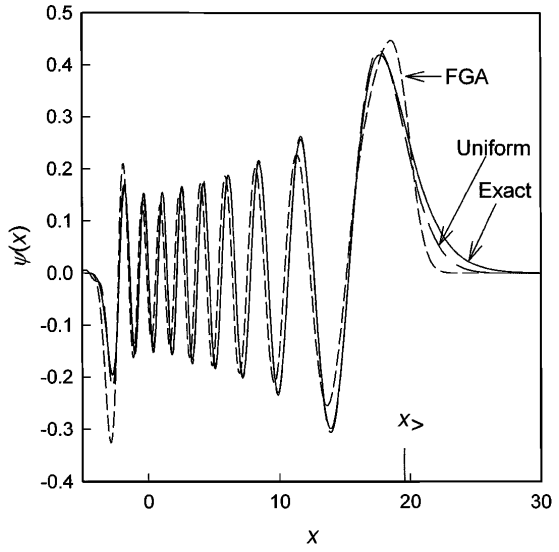

FIG. 3. Wave functions of the Morse oscillator for $n = 17$. Exact: solid lines, uniform semiclassical: long dashes; FGA: short dashes. $x_>$ is the maximum classical value of x.

One may suspect that this result signals the inability of the uniform approximation to treat even the "shallow" tunneling responsible for the tailing of wave functions into classically forbidden regions. However, the excellent quantum-semiclassical agreement that we have observed for the wave function tails of the quartic oscillator and the Morse oscillator at low energies argues against this conclusion. Instead, the observed inaccuracy is due to specific properties of the Morse system at energies near the dissociation limit. At such energies, $\dot{p}_t$ and $\dot{q}_t$ simultaneously become small as the particle approaches the right turning point since the derivative of the potential is itself small there. This causes the quantities z_{lm} to have large magnitudes, thus reducing the accuracy of the uniform approximation. As expected, the resulting inaccuracies are primarily reflected in the portions of the semiclassical wave functions near the turning point.

Although the behavior observed in Fig 3 does not imply the categorical failure of our approximation for the treatment of shallow tunneling, it does foreshadow such a breakdown for the description of "deep" tunneling between separate classically allowed regions. It is important to note that the inability to treat deep tunneling is not due to a breakdown in our proof that $(\hat{H} - E)\psi = O(\hbar^2)$. Instead, it arises because this condition is generally insufficient to guarantee that ψ is accurate in tunneling zones where the exact wave function vanishes more rapidly than any power of $\hbar$ in the classical limit. To treat deep tunneling, we must probably replace our real integration paths in Eq. (3) with appropriate complex contours [3].

Our numerical results illustrate the accuracy that can be achieved with the simple uniform approximation of Eq. (3) and suggest the suitability of this treatment for many applications [1–3]. For the case of constant γ, the uniform treatment can be regarded as a corrected version of the FGA. The correction found here is quite substantial and is expected to be even more important for multidimensional systems due to the lack of a relationship between the prefactors C_t and B_t in such cases. It is also worth mentioning that our uniform treatment links the FGA to the WKB approximation and helps elucidate the impressive success [14] of the FGA. We intend to present applications of the uniform approximation to multidimensional systems and explore different functional forms of γ in a separate publication.

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