Exact quantization of nonsolvable potentials: The role of the quantum phase

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Semiclassical quantization is exact only for the so-called *solvable* potentials, such as the harmonic oscillator. In the *nonsolvable* case, the semiclassical phase, given by a series in $\hbar$, yields more or less approximate results and eventually diverges due to the asymptotic nature of the expansion. A quantum phase is derived to bypass these shortcomings. It achieves exact quantization of nonsolvable potentials and allows us to obtain the quantum wave function while locally approaching the best predivergent semiclassical expansion. An iterative procedure allowing us to implement practical calculations with a modest computational cost is also given. The theory is illustrated on two examples for which the limitations of the semiclassical approach were recently highlighted: cold atomic collisions and anharmonic oscillators in the nonperturbative regime.

The semiclassical treatment of integrable systems, which can be traced back to Bohr's atomic model of planetary motion and Einstein's classic paper on the quantization of regular motion [1] is assumed to be a well established and venerable subject. In the standard semiclassical scheme [giving the Wentzel-Kramers-Brillouin (WKB) approximation that can be found in any standard textbook], the phase to be quantized is the classical action. Despite its usefulness, the WKB scheme often results in approximations that are quantitatively too crude and that fail to capture the physics of the problem. Indeed, WKB theory achieves exact quantization for a restricted number of potentials, such as the harmonic and Morse oscillators or the centrifugal Coulomb problem. In the last decade, the application of supersymmetric (SUSY) methods to quantum mechanics has enlarged the list of exactly quantized potentials to a handful of other potentials, quantized by employing SUSY WKB [2]. These potentials are sometimes qualified as "solvable" [3]. However, even in the solvable cases, the WKB wave functions are innaccurate especially at the turning points where they blow up, and a consistent divergence-free WKB scheme is still a topic of investigation [4]. In the more general nonsolvable case, WKB quantization has frequently resulted in useful approximations to compute the energy levels of excited states, but recently several shortcomings were pointed out: For example, the phase loss in the classically forbidden regions is badly taken into account by the WKB theory in potentials used in atomic clusters calculations [5]; in cold atom collisions WKB quantization breaks down for very excited states [6]; for anharmonic potentials, the failure of WKB has prompted extensive developments of numerically involved quantum techniques with the aim of obtaining accurate results (e.g., [7]).

We show in this work that these shortcomings can be resolved by considering an exact quantum phase. Phase functions in quantum mechanics can be arbitrarily defined through transformation functions, but theoretical as well as practical considerations require that the quantum phase bears a very close relationship to the semiclassical one. Let us take a one-dimensional conservative system at energy E in a single minimum potential well, which is our main concern in

this work. The WKB wave function is built from blocks given by

$$\psi_{\mathrm{WKB}}(x,E) = A(x,E)\exp[iS(x,E)/\hbar], \tag{1}$$

where the phase function $S(x,E)$ is the classical action and $A^2(x,E) = (\partial_x S)^{-1}$ gives the classical probability amplitude. The WKB quantization condition reads

$$S(t_2,E) - S(t_1,E) = \left(n + \frac{\mu}{4}\right)\pi\hbar, \tag{2}$$

where $t_{1,2}$ are the turning points, μ is the Maslov index (generally two in one-dimensional systems), and n is the level integer. To improve the approximation, a semiclassical expansion going beyond these purely classical terms can be carried out by going to higher order in $\hbar$. The procedure, based on a Riccati transform of the Schrödinger equation by which the term of order k depends on the derivatives of the terms of lower order, is well known [8,9] and will not be repeated here. The salient feature concerns the asymptotic nature of the expansion, which means that although going to higher order may improve the accuracy of the results, at some point the series generally diverge [9]. This is why in the present approach we will look for a quantum phase by directly starting from the Schrödinger equation

$$\hbar^2\partial_x^2 y(x) + p^2(x)y(x) = 0, \tag{3}$$

where $p(x)$ is the classical momentum. A transformation of the Liouville-Green type [10] is taken by writing

$$y(x) = [\partial_x\xi(x)]^{-1/2}w(\xi), \tag{4}$$

so that $\xi(x)$ appears as a "phase" and the prefactor as an amplitude, as in Eq. (1). Assume $w(\xi)$ fulfills the equation

$$\hbar^2\partial_\xi^2 w(\xi) + R(\xi)w(\xi) = 0, \tag{5}$$

where the choice of the unspecified function $R(\xi)$ determines the choice of w. ξ then obeys

$$R(\xi)(\partial_x \xi)^2 - p^2(x) + \frac{\hbar^2}{2}\langle \xi; x \rangle = 0, \tag{6}$$

where $\langle \xi; x \rangle \equiv \partial_x^3 \xi / \partial_x \xi - \frac{3}{2}(\partial_x^2 \xi / \partial_x \xi)^2$ denotes the Schwartzian derivative. The choice of the phase first depends on the choice of the carrier function w [or equivalently, of $R(\xi)$], and then on the choice of the boundary conditions that need to be imposed on the third order nonlinear Eq. (6). This is an illustration of the ambiguity suffered by phase functions in quantum mechanics, due here to the simple fact that there is no unique manner to cut a given wave function into a phase ξ on the one hand, and an amplitude function obeying the continuity equation $\alpha(x, E) = (\partial_x \xi)^{-1/2}$ (akin to the semiclassical case) on the other.

Formally, $\xi(x)$ can be expanded as an asymptotic series in $\hbar$,

$$\xi(x) = \sum_k \xi_{2k} \hbar^{2k}, \tag{7}$$

irrespective of the specific choice of R. But if we aim at making a connection with classical mechanics, it is apparent from Eq. (6) that the only choice that will give $\xi(x) \sim S(x)$ to first order in $\hbar$ corresponds to $R(\xi) = \pm 1$, leading by Eq. (5) to circular or exponential carrier functions. The price to pay is that the $\hbar$ expansion based on these functions, such as the WKB approximation, necessarily diverges at the turning points. However it must be noted that contrarily to the asymptotic expansions, the *exact* solutions do not diverge. It is thus natural to set $R = \pm 1$ and we will use the notation $\sigma(x)$ rather than $\xi(x)$ for this particular choice. Still, setting $R(\xi) = 1$ (as will be assumed in the remainder of this work) is not enough to lift the ambiguity of the phase. Mathematically speaking, the solutions of Eq. (6), for a given R, are distinguished by different boundary conditions. For arbitrary boundary conditions $\sigma(x)$ contains the oscillatory structure of the wave function $y(x)$, a fact that can be seen by calculating the derivatives $\partial_x^n \sigma$, which display violent oscillations. Of course the semiclassical series do not oscillate—neither the action S nor the higher order (in $\hbar$) semiclassical phase functions σ_{2k}, obtained by successive derivatives of S, present any type of oscillations. Therefore in order to represent the infinite order semiclassical expansion, we need a phase function free of oscillations. We draw here on previous work [11] where the following two points were discussed: (i) the classical action is the only first-order semiclassical phase that does not contain oscillatory structure, and (ii) a corresponding property holds for the quantum phase, i.e. there is a unique phase function that does not contain the quantum mechanical oscillatory structures. For solvable potentials it is possible to construct explicitly these optimal phase functions from the analytic solutions to Eq. (3) (e.g., parabolic cylinder functions for the harmonic oscillator, Whittaker functions in the centrifugal Coulomb case [12]). This is tantamount to choosing the appropriate boundary conditions of Eq. (6) at a *single* point (located in the classically allowed region). However for nonsolvable potentials, a procedure based on explicit analytic solutions does not exist. We can still follow the strategy employed for solvable potentials, focusing on obtaining

a numerical solution for the phase function (rather than analytical) by feeding boundary values at a given point that are an approximation of the optimal ones (rather than being exactly the optimal ones).

Before turning to the description of the method of calculation we recall the quantization condition in terms of σ, which contrary to Eq. (2) is exact. Let x span the interval $]s_1, s_2[$ (typically $]-\infty, +\infty[$ or $]0, +\infty[$ for radial problems). Let $\sigma(s_1) = 0$, and recall that α is a positive definite quadratic form that behaves as $\alpha(x \to s_{i=1,2}) \to \infty$ (see [11] and refs. therein). Since $y(x)$ is proportional to $\alpha(x)\sin\sigma(x)$ [Eq. (4)], the requirement that at the eigenvalues E we must have $y(s_2, E) \to 0$ gives the quantization condition in terms of the quantum phase

$$\sigma(s_2, E) = (n + 1)\pi, \tag{8}$$

where n is the level integer as in Eq. (2). Equation (8) holds irrespective of the boundary conditions imposed on σ. But when E is not an eigenvalue, $\sigma(s_2, E)$ depends on the arbitrary boundary condition and can take about any form in between two eigenenergies. This is in stark contrast with the semiclassical case given by the left-hand side of Eq. (2).

The computation of the exact quantum phase function $\sigma(x, E)$ is done by employing a numerical iterative scheme where the starting function is built from classical quantities. The iterative scheme is supplemented by semiclassical input in the form of boundary conditions. For reasons that will become clear below, the iterative scheme does not directly solve the highly nonlinear third-order differential Eq. (6), but applies to an equivalent first order yet complex differential equation. It can indeed be checked that by writing [we use atomic units (a.u.) from now on]

$$M(x, E) = \partial_x \left[\sigma(x, E) + \frac{i}{2}\ln(\partial_x \sigma) \right], \tag{9}$$

Eq. (6) leads to the first-order nonlinear differential equation

$$\partial_x M = i[p^2(x) - M^2(x)] \equiv \mathcal{F}(M(x), x), \tag{10}$$

where $\mathcal{F}$ denotes the middle term taken as a functional. Our strategy will consist of solving the equation for M; the real part will give us $\partial_x \sigma$, which can be numerically integrated to obtain σ, yielding both the wavefunction and the total phase $\sigma(s_2, E)$. To do so we first linearize the equation for M by expanding the functional to first order in the vicinity of an initial trial function $M_0(x)$. We then solve

$$\partial_x M_{q+1} = \mathcal{F}(M_q(x), x) + \left. \frac{\delta \mathcal{F}}{\delta M}\right|_{M_q} [M_{q+1}(x) - M_q(x)], \tag{11}$$

with $q = 0$ and where δ stands for the functional derivative. Equation (11) is a linear first-order differential equation that can be solved straightforwardly. Of course since $\mathcal{F}$ has been linearized Eq. (11) is not equivalent to Eq. (10), hence the subscript in M_1. Convergence toward M is achieved by iterating the procedure, i.e. we now solve Eq. (11) for $q = 1$, obtaining a better approximation M_2, and so on. This iterative linearization procedure, known as the quasilinearization

method (QLM) replaces the solution of a nonlinear differential equation by iteratively solving a linear one. It was introduced three decades ago by Bellman and Kalaba [13] in the context of linear programming, but the extension of QLM to the type of functions dealt with in quantum mechanics is quite recent [14].

To iteratively solve Eq. (11), two ingredients are needed: first the trial function $M_0(x)$, second, the boundary condition, $M_q(x_b)$, which is set from the start since it must be the same for each q. The choice of M_0, though mathematically unimportant, must correspond to the expected behavior of the converged solution. M_0 is thus built from first-order semiclassical functions. By inspecting how the real and imaginary terms behave to first order in $\hbar$, we are lead to setting

$$M_0(x,E) = |p(x)|\left[\theta(x-t_1)\,\theta(t_2-x) + i\,\theta(x-t_1) - i\,\theta(x-t_2)\right].$$
(12)

The boundary conditions are chosen so that M approximately represents the semiclassical series (for the real and imaginary terms) on the entire interval $]s_1,s_2[$. The simplest solution is to pick an arbitrary point x_b deep in the classically allowed region where the standard semiclassical expansion can be employed and go to the highest possible order in $\hbar$ before the series starts to diverge. For example, for the real part of M we have

$$\partial_x\sigma(x)|_{x=x_b} = \sum_{k=0}^{k\,\max} \partial_x\sigma_{2k}(x)|_{x=x_b}\hbar^{2k};$$
(13)

where k_{max} is set by going to the highest possible order before divergence occurs (with the choice of an appropriate terminant). More refined methods of estimating the optimal boundary condition, based on super- and hyper-asymptotic expansions [15], are, in principle, available. From a practical point of view, they are not necessary insofar as the behavior of σ, is barely affected by their use. Again, from a purely quantum mechanical perspective, all the quantum phases, irrespective of their behavior, lead to exact results.

We will now illustrate and detail the properties of the quantum phase on two specific examples. The first example concerns anharmonic oscillators which are employed in the investigation of many different phenomena, ranging from molecular vibrations to quantum field theories and phase transitions. This has generated different schemes to compute the eigenvalues and the wave functions, calling for large numerical basis or delicate resummation techniques [7]. The failure of the semiclassical approximation is important for the lowest levels: for example, for symmetric potentials x^{2m} WKB quantization gives the wrong behavior of the energies as a function of m. For anharmonic potentials $x^2+\lambda x^{2m}$, the accuracy of the WKB quantization decreases with increasing λ and m. Going to second order in $\hbar$ improves the quality of the semiclassical approximation, but the relative error is still high at low energies. For the lowest levels, the standard semiclassical expansion diverges beyond the second order. Alternative semiclassical expansions schemes such as the one based on the phase-integral method also break down for the lowest states [16]. Hence the interest in working with an exact quantum phase. Figure 1 shows the total phase $\sigma(s_2,E)$
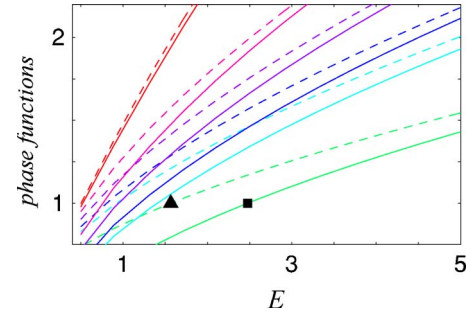

FIG. 1. (Color online) The total quantum phase $\sigma(s_2,E)/\pi$ (solid curves) is plotted along with the semiclassical quantization curve $[S(t_2,E)-S(t_1,E)]/\pi+1/2$ (dashed lines) for different values of λ: from left to right $\lambda=0.01$ (red), 1 (pink), 5 (purple), 20 (blue), 50 (light blue), and 1000 (green). The exact ground state energy for $\lambda=1000$ obtained by solving $\sigma(s_2,E)/\pi=1$ is shown by a box and the triangle shows the WKB quantized level off by 37%. Second-order quantization reduces the error to about 7% (depending on the terminant) and the $\hbar$ expansion diverges beyond this order.

at $s_2=\infty$ for anharmonic potentials $x^2+\lambda x^8$ at low energy for different values of λ. Given the symmetry of the potential, we have taken $x_b=0$ and fixed the value $M_0(x_b)$ by carrying out a semiclassical expansion up to $o(h^{14})$. The semiclassical phase is shown as well: Near the solvable potential limit $\lambda=0$ the quantum and semiclassical curves are very close, but as λ increases the degree of nonsolvability increases and the curves depart. This results in very inaccurate WKB quantization values, as compared to the exact ones obtained by applying the quantization condition (8).

The second illustration involves a potential well with a strong repulsion at short-range and a long-range attractive tail. These type of potentials are of interest in the study of cold atomic collisions, a field that has been sparked by the development of photoassociative spectroscopy. The WKB approximation breaks down for excited states near the threshhold because the wavefunction explores large areas of classically forbidden regions [6]. As in the first example, the standard semiclassical series diverge [17] and alternative expansions like higher order phase-integrals also break down [18]. We take the following 12-6 Lennard-Jones (LJ) potential with the classical momentum given in the scaled form as

$$p^2(x) = B\left[E - \left(\frac{1}{x^{12}} - \frac{2}{x^6}\right)\right],$$
(14)

where B is a "strength" parameter encapsulating the minimum and the depth of the potential well. This potential with $B=10^4$ has often been employed as a benchmark (see e.g., [17,18]) and is known to support 24 states. The WKB quantization condition (2) gives energies with an error relative to the local level spacing that globally increases with E. Figure 2 compares the derivative of the quantum phase $\partial_x\sigma(x,E)$ with the classical momentum $\partial_x S(x,E)$ for the last bound state just below the threshold. x_b was taken to the right of the potential minimum and the $\hbar$ expansion was carried out up to the 12th order. The two curves are barely distinguishable in the classically allowed region, so we have focused on the zone near the turning points. Note that the quantum curve
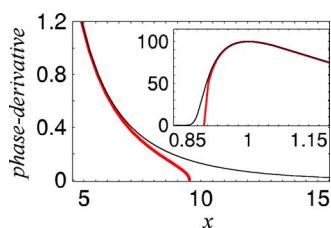
FIG. 2. (Color online) Derivative of the quantum phase $\partial_x \sigma$ (solid black curve) and of the classical action $\partial_x S = p$ (thick curve) in the 12-6 LJ potential characteristic of cold atom collisions (scaled a.u.). These quantities, plotted for the most excited bound state, are shown in the zone near the outer turning point $t_2 \approx 9.5$. The inset shows the zone near the inner turning point $t_1 \approx 0.9$ (note the very different scales).
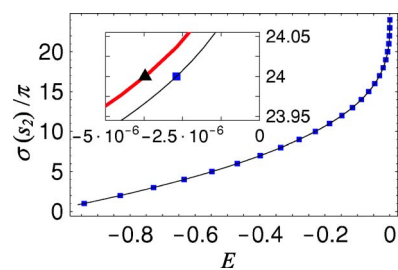

FIG. 3. (Color online) Exact energy levels (boxes) of the 12-6 LJ potential obtained by quantizing $\sigma(s_2, E)$ (solid curve), in scaled a.u. The inset zooms on the last state below threshold ($E=0$) and also shows the WKB prediction, about 40% too low (triangle).

largely penetrates into the classically forbidden region well beyond the outer turning point. This is typical of excited states in potentials with a long-range attractive tail and can be seen as the underlying reason ruling the breakdown of the semiclassical approximation. Quantization proceeds as above by determining $\sigma(s_2, E)$ on an energy grid, and then solving for Eq. (8). The resulting curve is shown in Fig. 3 and the quantized energies of the 24 levels exactly reproduce the values of exact quantum mechanical calculations [17]. In particular, the position of the last level determines the scat-

tering length, a crucial parameter in the production of Bose-Einstein condensates.

To summarize, we have employed a quantum phase that goes beyond the semiclassical approximation in giving the exact quantization energies as well as the wave functions. We have also given a numerical procedure to determine the phase based on the linearization of the phase equation and a boundary condition obtained from a local semiclassical expansion, and illustrated the approach in the case of two nonsolvable potentials.

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