Determination of bound-free dissociative couplings via classical Fourier coefficients

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This paper presents an approach to compute couplings between bound and unbound wave functions using only classical Fourier coefficients of the Hamiltonian. This approach is an extension of the well-known technique of using Fourier coefficients in the action-angle representation to compute bound-state to bound-state couplings. We develop the analogous bound-free approach for one-dimensional Hamiltonians and demonstrate it for several coupling potentials. The generalization to higher dimensions is also discussed. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Let $H(\boldsymbol{\phi},\mathbf{I})$ denote a D degree-of-freedom Hamiltonian expressed in some action-angle basis $(\boldsymbol{\phi},\mathbf{I})$, $\boldsymbol{\phi}\in[0,1]^D$. The EBK semiclassical quantization method associates a wave function with those actions $\mathbf{I}=(I_1,\ldots,I_D)$ satisfying $I_i=2\pi\hbar(n_i+\alpha_i/4)$, where each n_i is a non-negative integer, and the α_i denote the Maslov indices. Usually $\alpha_i=2$.

These semiclassical wave functions may be characterized by their quantum numbers $(n_1,\ \ldots,n_D)$, and give rise to a basis set $\{|n_1,\ldots,n_D\rangle\}$ which may be used in quantum calculations. The coupling between two semiclassical wave functions $|\mathbf{n}\rangle=|n_1,\ldots,n_D\rangle$ and $|\mathbf{m}\rangle=|m_1,\ldots,m_D\rangle$ is given by[1]

$$\langle\mathbf{m}|\hat{H}|\mathbf{n}\rangle=H_{\mathbf{m}-\mathbf{n}}\left(\frac{\mathbf{I_m}+\mathbf{I_n}}{2}\right). \tag{1}$$

$I_\mathbf{m}$, $I_\mathbf{n}$ denote the action vectors corresponding to the quantum numbers $\mathbf{m}$, $\mathbf{n}$, respectively, and $H_\mathbf{k}(\mathbf{I})$ denotes the $\mathbf{k}$ Fourier component of H evaluated at $\mathbf{I}$, defined via the expansion,

$$H(\boldsymbol{\phi},\mathbf{I})=\sum_{\mathbf{k}} H_\mathbf{k}(I)e^{2\pi i\mathbf{k}\cdot\boldsymbol{\phi}}. \tag{2}$$

This semiclassical coupling formula is well-known, and has proven useful in semiclassical approaches to the quantum dynamics of bound systems.[1–5]

What about dissociative processes? That is, given a bound-state and a continuum state which are both eigenstates of some zeroth-order Hamiltonian H_0, and a perturbation V, is it possible to express the V-induced dissociative coupling between the two in terms of the classical Fourier coefficients of V? Such a formula would be useful for extending semiclassical analyses based on classical Fourier coefficients to problems involving bond breaking (vibrational predissociation is one good example). Because semiclassical representations of the Hamiltonian based on classical Fourier coefficients grew out of the EBK method, these approaches required an action-angle representation of the Hamiltonian, and were therefore limited to bound–bound processes (since the action-angle basis is not defined in the scattering regime). In addition, the traditional focus within this area of semiclassical methods has been on energy spectra, so there has not been a major impetus to develop an analogous semiclassical formula for dissociative processes.

One natural approach in obtaining a semiclassical coupling formula would be to write down the WKB wave functions for both the bound and unbound wave functions, insert the potential V between them, and then attempt to perform the integration by stationary phase, in the hope that some kind of classical Fourier coefficient would naturally emerge. While appealing, such an approach will give no coupling, due to the lack of a stationary phase point. Indeed, the bound–bound coupling formula in an action-angle basis is derived by assuming that the two wave functions are close to each other in action, so that it is possible to linearize the difference between their corresponding classical action functions (which is obtained by solving the Hamilton–Jacobi equation at a given energy). The formal statement of the semiclassical coupling formula for action-angle variables is,

$$\lim_{\hbar\to 0}\langle I+2\pi\hbar k|\hat{V}|I\rangle=V_k(I) \tag{3}$$

where $|I\rangle,|I+2\pi\hbar k\rangle$ denote the semiclassical wave functions corresponding to actions $I,I+2\pi\hbar k$.

For unbound–unbound processes, Maitra and Heller[6] developed an approach based on the use of WKB wave functions as a distorted-wave basis. Specifically, they considered the problem of above-barrier reflection in one dimension, and showed that the use of the WKB wave functions worked well at essentially all above-barrier energies as a distorted-wave basis in the first-order Born approximation. While their coupling formula was not given in terms of classical Fourier coefficients of the Hamiltonian, it is possible to show that, in a sufficiently semiclassical limit, the coupling formula may be given in such a form. Maitra and Heller discussed the idea of obtaining a general method to assign a semiclassical quantum coupling between any two contours in phase-space. In particular, such a formula would include the ability to compute couplings between wave functions corresponding to bound and unbound phase-space contours.

The difficulty in generalizing the bound–bound coupling formula to the bound-free case is that there is a sudden change in the topology of the phase-space in going from the bound regime to the unbound regime. In the bound regime it is possible to semiclassically characterize the wave functions by quantum numbers corresponding to definite values of the classical action, while in the unbound regime this is not possible. Thus, it is not immediately obvious in what canonical basis to Fourier expand the Hamiltonian.

One approach that might work is to express the coupling as a Fourier transform of $V(\mathbf{q}(t))$, where $\mathbf{q}(t)$ denotes the ordinary position representation of a trajectory generated by the zeroth-order Hamiltonian H_0. Such an approach is related to semiclassical theories based on the Fourier analysis of classical quasiperiodic motion (see Ref. 7 for a review of such methods). Since such a Fourier analysis obviates the need to find an action-angle representation of the Hamiltonian (which does not exist in the unbound regime), it is possible that this approach may be tailored to determine semiclassical bound-free couplings.

This paper develops a bound-free semiclassical coupling formula based on the Fourier analysis of classical motion. The resulting coupling formula is shown to be the analogous expression to the one obtained in the action-angle representation. We initially derive the coupling formula for one-dimensional systems, but then go on to generalize it to D-dimensional systems.

This paper is organized as follows: In Sec. II, we develop the one-dimensional system which we will consider. We go on in Sec. III to construct the semiclassical bound and unbound states, and obtain the semiclassical coupling between them. We test our formula with some numerical examples in Sec. IV. We discuss how the coupling formula may be generalized and applied to dissociation processes in Sec. V. Finally, we present our conclusions in Sec. VI.

II. THE HAMILTONIAN

Consider the one-dimensional Hamiltonian,

$$H_0(q,p)=\frac{p^2}{2m}+V(q). \tag{4}$$

We assume that V has the following properties: (1) $\lim_{q\to-\infty} V(q)=\infty$; (2) $\lim_{q\to\infty} V(q)=V_0$; (3) V attains its global minimum at some $q_{\min}$, and is monotone decreasing for $q<q_{\min}$ and monotone increasing for $q>q_{\min}$.

The Morse oscillator $(V(q)=D(1-e^{-\beta x})^2)$ is a good example of such a system. Such a Hamiltonian admits bound states up to the dissociation energy V_0, and outgoing states above V_0. Below V_0, we may assume that the bound-states are given by quantum numbers $\{n\}$, corresponding to actions $I_n=2\pi\hbar(n+\frac{1}{2})$, according to WKB theory in one dimension. Above V_0, the Hamiltonian admits outgoing states for all energies $E>V_0$.

Suppose we add a perturbative potential $V^{(1)}(q)$ which can induce couplings between the eigenstates. Our goal is to write down a semiclassical expression for $\langle E|\hat{V}^{(1)}|n\rangle$, where $|E\rangle$ denotes an outgoing state, and $|n\rangle$ denotes a bound state. We do this in the following section.

III. THE COUPLING FORMULA

A representation which is ideally suited to the Hamiltonian H_0 is the energy-time representation. In this canonical basis, the canonical momentum is given by the energy $E=H_0(q,p)$, and the canonical position is the transit time from the inner turning point at energy E to (q,p). If we define $t(E)$ to be the time it takes a trajectory to go from the inner turning point to the outer turning point at energy E, then any point on the $H_0(q,p)=E$ phase-space contour may be uniquely characterized by some $t\in[-t(E),t(E)]$. Of course, if E is above dissociation, then $t(E)=\infty$. Because $(\pm t,E)$ represents some $(q,\pm p)$, it follows that in the energy-time representation of $V^{(1)}(q)$ we have $V^{(1)}(t,E)=V^{(1)}(-t,E)$.

The generating function from the (q,p) system to the (t,E) system is given via,

$$S(q,E)=\int_{q^-(E)}^{q} p(q',E)\,dq', \tag{5}$$

where $q^-(E)$ denotes the inner turning point at energy E, and p denotes the momentum, given by $p(q,E)=\sqrt{2m(E-V(q))}$. The conversion from the (q,p) to the (t,E) representation may be obtained from the equations,[8]

$$p(q,E)=\frac{\partial S}{\partial q}(q,E), \tag{6}$$

$$t(q,E)=\frac{\partial S}{\partial E}(q,E). \tag{7}$$

It may be simply shown that $t(q,E)$ is the time it takes for a particle starting at the inner turning point at energy E to reach the point q. In contrast to the (ϕ,I) representation, the (t,E) representation can be used to represent both the bound and unbound eigenfunctions of H_0. The WKB wave functions are real and may be given by

$$\psi_E(q)=A(E)\sqrt{\left|\frac{\partial^2 S}{\partial q\,\partial E}\right|}(\exp[iS(q,E)/\hbar] + \exp[-iS(q,E)/\hbar]), \tag{8}$$

where $A(E)$ is some normalization constant which we will be given later. In reality, this formula breaks down near the turning points. However, in the semiclassical limit we will assume (as with the analogous derivations for the case of action-angle representations) that only contributions from the classically allowed region are important, in which case the above formula holds.

If $E<V_0$, then $E=E_n=H_0(I_n)$, and we want the normalization $\langle n'|n\rangle=\delta_{nn'}$. It is a standard semiclassical result that this requires $A_n\equiv A(E_n)=\sqrt{\nu(I_n)}$, where $\nu(I_n)\equiv dE/dI|_{I_n}$ is the frequency at I_n. For the outgoing states, we want $\langle E'|E\rangle=\delta(E-E')$, giving $A(E)=1/\sqrt{2\pi\hbar}$.

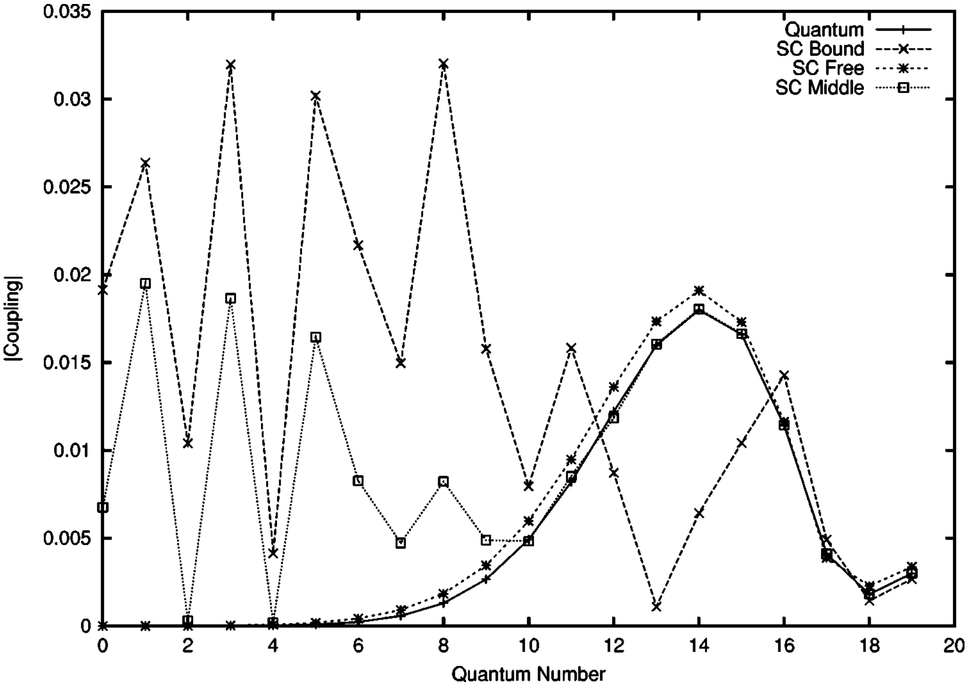

FIG. 1. Quantum vs semiclassical coupling for $\alpha=0.01$.

We now derive the semiclassical coupling between the bound-state $|n\rangle$ and the outgoing state $|E\rangle$. Analogous to the derivation of the bound–bound formula, we assume that $E \approx E_n$. Consider, then, some energy $E_m \in [E_n, E]$. We can then write $S(q,E)-S(q,E_n) \approx \partial S/\partial E|_{E_m}(E-E_n)$. Then we integrate from the inner turning point $q^-(E_m)$ to the outer turning point $q^+(E_m)$, where $q^+(E_m)$ may very well be ∞ if $E_m > V_0$. The semiclassical coupling is then,

$$\begin{aligned}\langle E|\hat{V}^{(1)}|n\rangle &= \sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\int_{q^-(E_m)}^{q^+(E_m)} dq' V^{(1)}(q')\left|\left(\frac{\partial^2 S}{\partial q'\partial E}\bigg|_{E_m}\right)\right| \\ &\quad \cdot e^{i(\partial S/\partial E)|_{E_m}(E-E_n)/\hbar}+e^{-i(\partial S/\partial E)|_{E_m}(E-E_n)/\hbar} \\ &= \sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\int_0^{t(E_m)} dt V^{(1)}(t,E_m)(e^{i(E-E_n)t/\hbar} \\ &\quad + e^{-i(E-E_n)t/\hbar}) \\ &= \sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\int_{-t(E_m)}^{t(E_m)} dt V^{(1)}(t,E_m)e^{-i(E-E_n)t/\hbar} \\ &= \sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\tilde{V}^{(1)}_{(E-E_n)/2\pi\hbar}(E_m). \end{aligned} \tag{9}$$

Thus, the semiclassical coupling $\langle E|\hat{V}^{(1)}|n\rangle$ between the bound state $|n\rangle$ and the outgoing state $|E\rangle$ is given by,

$$\langle E|\hat{V}^{(1)}|n\rangle = \sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\tilde{V}^{(1)}_{(E-E_n)/2\pi\hbar}(E_m), \tag{10}$$

where

$$\tilde{V}^{(1)}_k(E) \equiv \int_{-t(E)}^{t(E)} dt V^{(1)}(t,E)e^{-2\pi ikt}. \tag{11}$$

We have an expression for the bound-free coupling in terms of the Fourier coefficients of $V^{(1)}$ in the energy-time basis. The coupling is given by a Fourier component of $V^{(1)}(q(t))$, where $q(t)$ denotes a classical trajectory generated by the zeroth-order Hamiltonian H_0. Note that the coupling formula is analogous to the corresponding formula for action-angle variables, but instead with time and energy playing the roles of the canonical position and momentum, respectively.

IV. NUMERICAL TESTS

We tested our coupling formula numerically for the zeroth-order Hamiltonian,

$$H_0(q,p) = \frac{p^2}{2\mu} + D(1-e^{-\beta q})^2 \tag{12}$$

using $V^{(1)}(q)=e^{-\alpha q^2}$. H_0 has a zeroth-order harmonic frequency ω_0 given by $\frac{1}{2}\mu\omega_0^2 = D\beta^2$. We took $\mu=1.0$, $\omega_0=1.0$, $D=10.0$, and $\hbar=1.0$. This Hamiltonian supports 20 bound states, with energies given by, $E_n=(n+\frac{1}{2})\hbar\omega_0(1-[(n+\frac{1}{2})\hbar\omega_0/4D])$, where $n=0, 1, 2, \ldots, 19$.

Figures 1–4 plot the couplings between all the bound-states to the outgoing state with energy $E=11.0$, for $\alpha=0.01$, 0.1, 1.0, and 10.0, respectively. Three values of E_m were used: $E_m=E_n$, the energy of the bound-state; $E_m=E$, the energy of the outgoing state; and $E_m=(E_n+E)/2$, the energy midway between the two states.

We may note for all four graphs, that, as the quantum number increases, the semiclassical couplings all converge on the quantum result, which is to be expected, since at higher energy the semiclassical approximation, as well as the linearization of the generating function S, become more accurate. Nevertheless, we may note that certain choices for E_m are better than others depending on the potential.

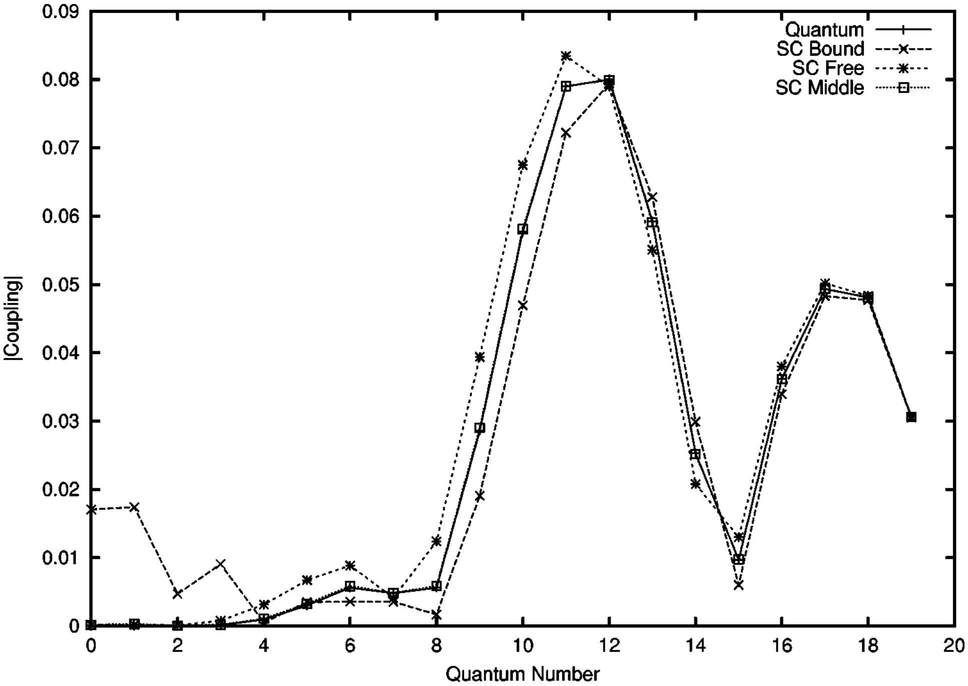

FIG. 2. Quantum vs semiclassical coupling for $\alpha = 0.1$.

For $\alpha = 0.01$, the $E_m = E$ graph (''SC free'') is quantitative over the entire range of bound-states. The $E_m = (E_n + E)/2$ graph (''SC middle'') only becomes quantitative for bound-states with quantum numbers around 10 or higher. The $E_m = E_n$ graph (''SC bound'') takes the longest to become quantitative, at a quantum number of 16.

For $\alpha = 0.1$, all graphs remain fairly quantitative, except for $E_m = E_n$ for $n \in [0,4]$. The best fit is for $E_m = (E_n + E)/2$, which is essentially indistinguishable from the quantum result.

A similar pattern persists for $\alpha = 1.0$, though this time the ''SC bound'' and ''SC free'' graphs take somewhat longer to become quantitative than previously. Nevertheless, the ''SC middle'' graph remains quantitative for all quantum numbers.

Finally, for $\alpha = 10.0$, we see that all three semiclassical graphs become quantitative around $n = 5$, though once again it appears that the ''SC middle'' graph is more accurate than the rest.

There are several patterns to note here. First of all, of the three prescriptions for choosing E_m, the choice $E_m = (E_n + E)/2$ was the most accurate, with the notable exception for $\alpha = 0.01$, for which $E_m = E$ was the most accurate. Both results are easy to explain. In general, using $E_m = (E_n + E)/2$

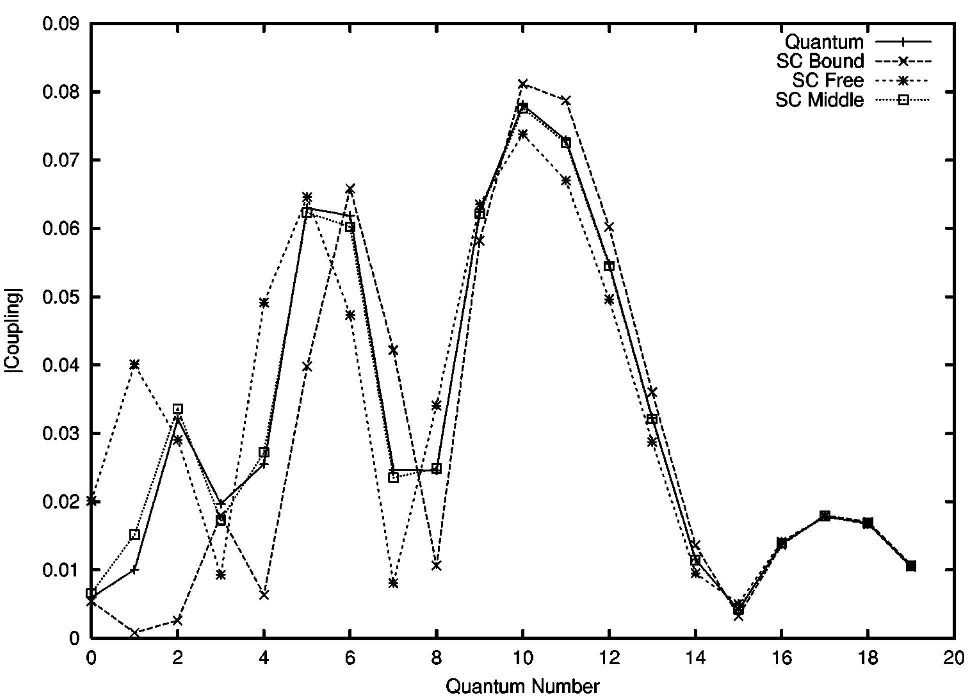

FIG. 3. Quantum vs semiclassical coupling for $\alpha = 1.0$.

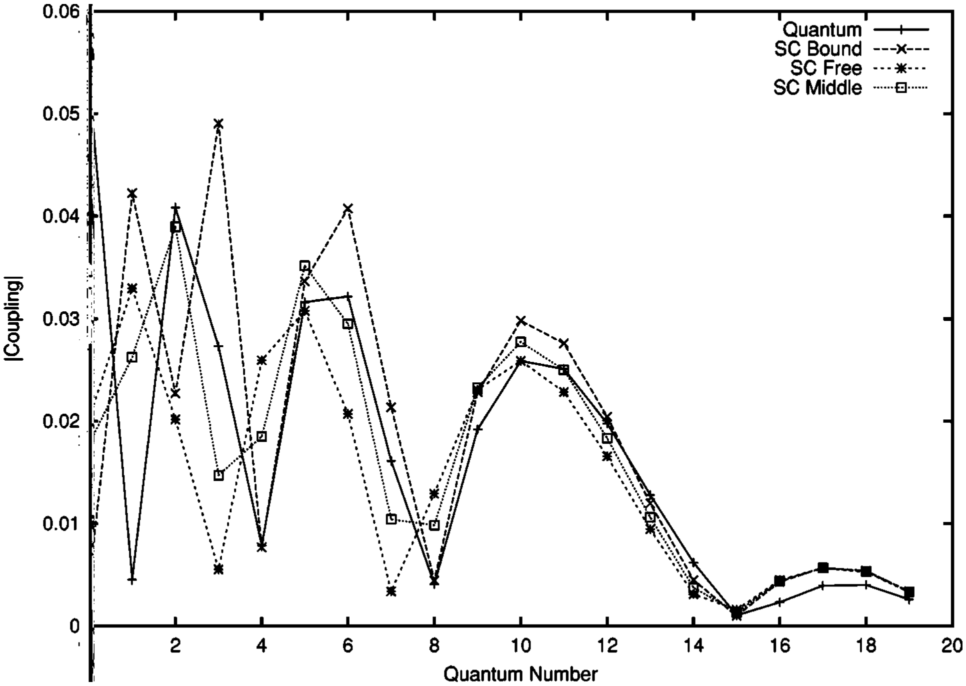

FIG. 4. Quantum vs semiclassical coupling for $\alpha=10.0$.

should be more accurate than using $E_m=E_n$ or E, because the expression $S(q,E)-S(q,E_n)=(\partial S/\partial E)(q,E_m)(E-E_n)$ is accurate to third-order in $E-E_n$ for $E_m=(E_n+E)/2$, but only accurate to second-order in $E-E_n$ for $E_m=E_n,E$. In the case of $\alpha=0.01$, however, the potential is sufficiently spread out that using $E_m=E_n,(E+E_n)/2$ results in integration over too narrow a range for the lower quantum numbers to accurately capture all the coupling. Because for $E_m=E$ the integration range is infinite, it captures the whole potential, leading to a more accurate expression for the coupling.

Finally, while the semiclassical coupling graphs for $\alpha=0.01$, 0.1, 1.0 become essentially indistinguishable from the quantum results for the higher quantum numbers, a small discrepancy persists for $\alpha=10.0$ all the way up to $n=19$. The reason for this is that the potential at this point is so narrow that the effective integration range for the coupling is fairly narrow. However, semiclassical approaches are expected to be accurate in regimes where $\hbar$ is small, or equivalently, when the characteristic wavelength is short compared to the length scales of the problem. In this case, the effective range of the potential is sufficiently short that it leads to observable (though small) discrepancies between the quantum and semiclassical results.

V. APPLICATION TO DISSOCIATION PROCESSES

While the bound-free semiclassical formula was developed for one-dimensional systems, the generalization to separable systems is immediate. Specifically, given a D degree-of-freedom Hamiltonian,

$$H_0(q_1,\ldots,q_D,p_1,\ldots,p_D)=\sum_{i=1}^{D}\left(\frac{p_i^2}{2\mu_i}+V_i(q_i)\right) \tag{13}$$

which produces an energy-time representation of phase-space given by $(t_1,\ldots,t_D,E_1,\ldots,E_D)$, then given some potential $V^{(1)}(q_1,\ldots,q_D)$ we obtain the semiclassical result,

$$\langle E_1,\ldots,E_D|\hat{V}^{(1)}|n_1,\ldots,n_D\rangle = (2\pi\hbar)^{-(D/2)}\sqrt{\prod_{i=1}^{D}\nu(I_{n_i})}\,\tilde{V}^{(1)}_{(\mathbf{E}-\mathbf{E_n})/2\pi\hbar}(\mathbf{E_m}), \tag{14}$$

where $\mathbf{E}\equiv(E_1,\ldots,E_D)$, $\mathbf{E_n}\equiv(E_{n_1},\ldots,E_{n_D})$, and $\mathbf{E_m}\equiv(E_{m_1},\ldots,E_{m_D})$.

For nonseparable systems, the formula is in principle the same, as long as it is possible to find a canonical representation of the phase space which can be used to construct the semiclassical basis functions in both the bound and unbound regimes.

To illustrate how the semiclassical bound-free formula may be used, we consider a simple example of a two-dimensional dissociative process from some bound state $|v\rangle|E_n\rangle$ to an unbound state $|v-1\rangle|E\rangle$. This process corresponds to a vibrational predissociation process, where one quantum of vibration (the "v" states) is transferred to a translational degree of freedom, with sufficient energy to cause dissociation. If we assume that bound states have the $\delta_{nn'}$ normalization, and unbound states have the $\delta(E-E')$ normalization, then if V denotes the perturbation leading to dissociation, the dissociative coupling is given semiclassically by

$$\langle v-1,E|\hat{V}|v,E_n\rangle=\sqrt{\frac{\nu(I_n)}{2\pi\hbar}}\tilde{V}_{(-1,(E-E_n)/2\pi\hbar)}(2\pi\hbar v,E_m). \tag{15}$$

Here $\tilde{V}$ denotes the Fourier expansion of V, where the vibrational coordinates are expanded in action-angle variables, and the translational coordinates are expanded in an energy-time representation. $\nu(I_n)$ denotes the zeroth-order frequency for the translational motion in the bound-state with quantum number n. Applying Fermi's Golden Rule, we then obtain a dissociation rate into the $|v-1,E\rangle$ unbound state of,

$$\Gamma_{v\rightarrow v-1}=\frac{2\pi}{\hbar}|\langle v-1,E|\hat{V}|v,E_n\rangle|^2. \tag{16}$$

The type of vibrational predissociation process described above does not include rotational effects. Thus, what we have presented is a simplification of the true predissociation dynamics. Nevertheless, the purpose is to give a concrete example, illustrating how the bound-free semiclassical coupling formula may be applied to actual systems.

VI. CONCLUSIONS

This paper presents a semiclassical approach for computing the bound-free couplings for one-dimensional systems based on a Fourier analysis of classical trajectories. The result is a generalization of the formula for bound–bound couplings. The key difference is that while the bound–bound couplings are generally given as Fourier coefficients from an action-angle representation of the Hamiltonian, in the bound-free case the Fourier coefficients come from an energy-time representation of the Hamiltonian. Such a representation is valid in both the bound and unbound regimes, though the range of the time variable is energy-dependent (in contrast to action-angle variables, for which the range of the angle variable is an interval of length 1). Numerical tests for several potentials confirmed the semiclassical formula.

The bound-free semiclassical coupling formula could prove useful in analyzing a variety of dissociation processes. A simple example involving vibrational predissociation was given in the previous section. Because the semiclassical couplings are obtained from Fourier coefficients of a classical Hamiltonian, they are in general easier to compute than the quantum couplings, which would require the numerical integration of wave functions.

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