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Quantum-Classical Correspondence for the Fourier Spectrum of a Trajectory

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In this paper, we shall address the question of classical-quantum correspondence of the Fourier spectrum of a classical variable. An example of such a variable from classical mechanics is

$$X_\omega = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} X_t dt, \qquad (1)$$

where X_t is the x-coordinate as a function of time. In systems of interest, X is but one of several coordinates, and the dynamics may be integrable or chaotic . Such Fourier spectra are often used as qualitative indicators of chaos, because in the quasiperiodic region, only N fundamental frequencies (ω_{01} --- ω_{0N}) and the their overtones and combinations may appear in $X\omega$:

$$X_\omega = \sum_{\underset{\sim}{m}} X_{\underset{\sim}{m}} \delta(\omega - \underset{\sim}{m}\cdot\underset{\sim}{\omega}_0) \quad , \qquad (2)$$

whereas in the chaotic domain, no such restrictions apply.

A quantum analog of Eq. (1) is obtained by replacing X_t with X_t^0 where $X_t^0 = \langle X \rangle_t = \langle \psi_t | X | \psi_t \rangle$. It is an interesting exercise to discover how the classical limit, Eq. (2) is recovered from the quantum mechanics as $\hbar \to 0$, and how the classical chaos is reflected in the quantum spectra.

In order to correspond to the classical situation of setting all the initial conditions of the coordinates and momenta to some specified values, and "running a trajectory" to determine X_t, we take the initial wavefunction ψ_0 to be as localized as possible in phase space. An ideal way to do this is with the coherent states (gaussian wavepackets) $|q_0(X_0,P_0)\rangle$, which are minimum uncertainty states with

$$\langle g_o | \underset{\sim}{X} | g_o \rangle = X_o$$
$$\langle g_o | \underset{\sim}{P} | g_o \rangle = P_o \qquad (3)$$

Ehrenfest's theorem tells us that X_t and X_t^Q will be nearly the same for some reasonable time, this time becoming longer as $\hbar \to o$. This simple fact already implies a limited kind of quantum-classical spectral correspondence, because of a certain property of the Fourier convolution theorem which we might call "enveloping." Consider two trajectories, X_t and X_t^Q for which we may say

$$X_t \simeq X_t^Q , \qquad |t| \underset{\sim}{<} \tau \quad . \qquad (4)$$

For $|t| > \tau$, suppose no claim is made as to the proximity of X_t and X_t^Q. Now consider

$$X_\omega = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} \, X_t \, dt \qquad (5)$$

with a similar equation for X_ω^Q, and

$$\bar{X}_\omega = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} \, C_t \, \lambda_t \, dt \qquad (6)$$

with a similar equation for $\bar{X}_\omega^Q$, and where C_t has the property

$$C_t \simeq 1 \quad |t| < \tau \tag{7}$$
$$\simeq 0 \quad |t| > \tau$$

With the conditions (4) and (7), we have immediately

$$\bar{X}_\omega \simeq \bar{X}^Q_\omega \tag{8}$$

The Fourier convolution theorem dictates

$$\bar{X}_\omega = \frac{1}{\sqrt{2\pi}} \int d\omega' \, C_{\omega'} X_{\omega-\omega'} \tag{9}$$

with an analogous equation for $\bar{X}^Q_\omega$.

The Fourier transform of C_t, namely C_ω, has a spectral width of $\Delta\omega \simeq 2\pi/\tau$. Equations (8) and (9) thus dictate that, whatever the differences in the detailed, high resolution X_ω and X^Q_ω, the smoothed (convoluted) versions $\bar{X}_\omega$ and $\bar{X}^Q_\omega$ have to agree with each other up to a resolution $\Delta\omega$, if X_t and X^Q_t agree up to a time τ, where $\Delta\omega\tau \simeq 2\pi$.

In a loose sense, we may say that the spectrum X_ω must be consistent peak its low resolution analog, $\bar{Y}_\omega$, in which accumulations of intensity may be smoothed into bands at lower resolution.

Figure 1 with help to illustrat the situation. The left sequence show the quantum spectrum $\bar{X}^Q_\omega$ for τ increasing downward, the right sequence show the classical spectrum, $\bar{X}_\omega$. For t longer than τ, X_t and X^Q_t start to deviate, and the quantum spectrum starts to show sub-bands not present in the classical spectrum. The classical spectrum simply narrows around the allowed Fourier components of the quasiperiodic motion.

So far, we have only required Fourier analysis and Ehrenfest's theorem, and a certain spectral similarity of $\bar{X}_\omega$ and $\bar{X}^Q_\omega$ has been noted. To understand the sub-structure present in the higher resolution quantum spectrum $\bar{X}^Q_\omega$, we must introduce a little quantum (or at least semiclassical) mechanics. Two features are present in each of the quantum clusters of lines: 1) The width of the cluster, 2) the number of peaks in each cluster.

Evidently, the width of the cluster, $\Delta\omega$, is directly related to the time, τ, after which the classical and quantum dynamics X_t and ${}^QX_t$ start to differ; i.e., $\Delta\omega\ \tau \simeq 2\pi$. However, this observation is more tautology than anything else. What is needed is a basis for understanding or predicting the magnitude of τ or $\Delta\omega$.

Specializing to one degree of freedom we examine

$$X^Q_t = \langle g_t | X | g_t \rangle \tag{10a}$$

$$= \langle g_o | e^{iHt/\hbar} X\, e^{-iHt/\hbar} | g_o \rangle \tag{10b}$$

$$= \sum_{nn'} f^*_n X_{nn'} f_{n'}\, e^{-i(E_{n'}-E_n)t/\hbar} \tag{10c}$$

where $\langle g_o | n \rangle = f^*_n$ etc., and $|n\rangle$ are eigenstates. Also,

$$X^Q_\omega = \sum_{nn'} f^*_n X_{nn'} f_{n'}\, \delta(\omega - \Delta_{nn'}) \tag{11}$$

where $\Delta_{nn'} \equiv (E_{n'}-E_n)/\hbar$. The factors contributing to the overall appearance of X_ω are the quantities f_n, E_n, and $X_{nn'}$. We examine each of these in turn.

In one degree of freedom for a bound potential, the main qualitative feature of the f_n's is a smoothly peaked pattern of intensity. The f_n's for a harmonic oscillator potential follow a Poisson distribution, tending to Gaussian as the displacement of $|g_o\rangle$ gets greater.[2] The overall energy spread is

$$\Delta E \sim \left(\frac{dV}{dx}\right)_{x=x_o} \sqrt{\frac{\hbar}{m\omega_c}} \tag{12}$$

where the gaussian g_o is of the form

$$g_o(x) = \left(\frac{m\omega_o}{\pi\hbar}\right)^{1/2} e^{\frac{-m\omega_o}{2\hbar}(x-x_o)^2}$$

and V(x) is the potential energy. The distribution of fn's always becomes gaussian as $\hbar \to o$, or as the displacements get large.

Now consider the energies E_n of the states. Let us take an energy near the center of the f_n distributions, call this E_p. The action[4] of this state is

$$j_p = (p+\tfrac{1}{2})h \tag{13}$$

The hamiltonian H is expandable in term of the action as

$$H(j) = H(j_o) + \partial H/\partial j\big|_{j=j_o} (j-j_o) + \frac{1}{2}\,\partial^2 H/\partial j^2\big|_{j=j_o} (j-j_o)^2 + \cdots \tag{14a}$$

$$= E(j_o) + \nu(j_o)\,(j-j_o) + \frac{1}{2}\,\frac{\partial \nu}{\partial j}\Big|_{j=j_o} (j-j_o)^2 + \cdots, \tag{14b}$$

where ν is the classical frequency of motion. Applying these relations to the present situation we have, semiclassically,

$$E_n = E_p + \hbar\omega_p(n-p) + \frac{\hbar}{2}\omega_p'(n-p)^2 + \cdots \tag{15}$$

where $H(j_p) \equiv E_p$, $\omega(j_p) \equiv \omega_p$, $h\left.\frac{\partial\omega}{\partial j}\right|_{j=j_p} \equiv \omega_p'$.

Note that because of the factor h in the definition of ω_p', $\omega_p' \to o$, as $h \to o$, since $\omega(j)$ is a purely classical quantity. Thus Eq. (15) is a statement of the Bohr Correspondence Principle, namely,

$$E_{n+1} - E_n \simeq \hbar\omega_{\bar{n}} \tag{16}$$

where $\omega_{\bar{n}}$ is the classical frequency of motion at the average value of the action

$$\bar{j} = \frac{(n+1+\frac{1}{2})+(n+\frac{1}{2})}{2}\, h = (n+1)h \tag{17}$$

The last quantity we need to study is $X_{nn'}$. Standard semiclassical tricks (See the Appendix) give

$$X_{nn'} \sim \int_o^{2\pi/\bar{\omega}} e^{i\Delta_{nn'}t} X_t \, dt \tag{18}$$

where $\bar{\omega}$ is the frequency at the average action $\bar{j}$ and X_t is the classical trajectory. As $|n-n'|$ gets large, $X_{nn'}$ is expected to get small, since the Fourier frequency, $\Delta_{nn'} = (E_n - E_{n'})/\hbar \simeq \bar{\omega}(n-n')$, gets large.

The spectral features corresponding to n'-n =m are distinct for each m. Let us consider m=1 first (the "fundamental"). For n'=n+1 (n'=n-1 is the negative frequency range), we have

$$X^Q_\omega = \sum_n f^*_n \; X_{nn+1} \; f_{n+1} \delta(\omega-\omega_p-\omega'_p(n-p+\tfrac{1}{2})) \tag{19}$$

For small $\hbar$, $f^*_n f_{n+1} \simeq |f_n|^2$ since the f_n's vary smoothly, and from Eq. (18) we have

$$X_{nn+1} \simeq X_1, \tag{20}$$

where X_1 is the classical fundamental intensity. These observations yield, for this fundamental,

$$X^Q_\omega \simeq X_1 \sum_n |f_n|^2 \; \delta(\omega-\omega_p-\omega'_p(n-p+\tfrac{1}{2})) \tag{21}$$

Already some interesting facts are emerging. First, since $\sum_n |f_n|^2 = 1$, the integral <u>intensity</u> of the quantum fundamental band equals the classical intensity of the fundamental. Second we can calculate the <u>width</u> of the quantum fundamental band of lines as follows. From Eqs. (12) and (14) we have

$$\begin{aligned} \Delta E &= \left(\frac{dV}{dx}\right)_{x=x_o} \sqrt{\frac{\hbar}{m\omega_o}} \\ &= \nu \, \Delta j = \omega_p (n^+ - n^-) \; ; \\ &\equiv \hbar\omega_p \Delta n \end{aligned} \tag{22}$$

where n^+ and n^- are the values of the quantum number n at the FWHM of the $|f_n|^2$ distribution. Equation (22) gives

$$\Delta n = \left(\frac{dV}{dx}\right)_{x=x_o} \sqrt{\frac{\hbar}{m\omega_o}} \cdot \frac{1}{\hbar\omega_p} \tag{23}$$

The frequency spread of the band is

$$\Delta\omega = h\left(\frac{d\omega}{dj}\right)_{j=j_p} \Delta n \tag{24}$$

This gives, for $\Delta\omega$,

$$\Delta\omega = \sqrt{\frac{\hbar}{m\omega_o}} \left(\frac{d\omega}{dj}\right)_{j=j_p} \left(\frac{dV}{dx}\right)_{x=x_o} \nu_p^{-1} \quad .$$

The time at which x_t and x_t^Q start to differ by the arguments gives above, is

$$\tau = 2\pi/\Delta\omega$$

We see that

$$\tau \propto \nu_p, \left(\frac{dV}{dx}\right)^{-1}_{x=x_o}, \left(\frac{d\omega}{dj}\right)^{-1}_{j=j_p}, \omega_o^{1/2}, \hbar^{-1/2} \quad .$$

That is, the correspondence between the classical and the quantal x_t and x_t^Q lasts longer if 1) the classical frequencies is higher, 2) the potential slope near the wavepacket is smaller, 3) the rate of change of classical frequency with action is smaller, 4) a larger ω_o is used in the wavepacket, and 5) $\hbar \to o$. All these trends will hold in the $\hbar \to o$ limit. Now, from Eq. (23) we see that $\Delta n \propto \hbar^{-1/2}$, i.e., the quantum number spread of the wavepacket is <u>increasing</u> as $\hbar \to o$, and $\Delta\omega \propto \hbar^{1/2}$, i.e., the frequency spread of the fundamental quantum based of lines is <u>decreasing</u> as $\hbar^{1/2}$ as $\hbar \to o$.

From Eq. (21), we see that

$$X_\omega^Q \xrightarrow{\hbar \to 0} X_\omega \ , \tag{24}$$

since the intensity, the frequency, and the width of the overtone band all agree with the classical result as $\hbar \to 0$.

The analysis for an overtone band, m=2,3,... is much the same as for the fundamental band just presented.

The extension of the present result to two and more degrees of freedom is quite easy in the quasiperiodic domain of the classical mechanics. The results are the same; around each sharp classical fundamental, overtone, or combination line a quantum cluster of lines exist. The number of lines in the cluster increases as $\hbar^{-1/2}$ as $\hbar \to 0$, but the width of these cluster decreases as $\hbar^{1/2}$.

For an anharmonic n- dimensional system, a particular classical trajectory of a given energy E and action variables $j_1, j_2, \ldots j_N$ has a given discrete set of fundamental frequencies $\omega_1 \ldots \omega_N$. These frequencies, and their overtone and combinations, appear in X_ω. However, at the same energy, another set of actions $j_1', j_2' \ldots j_N'$ would give in general a different set of classical frequencies, $\omega_1', \ldots, \omega_N'$. In a certain sense, there are "missing" frequencies in a Fourier spectrum of any given quasiperiodic classical trajectory because the N actions $j_1 \ldots j_N$, are conserved in the dynamics, preventing other frequencies from making an appearance. As $\hbar \to 0$ these statements apply to the quantum clusters of lines: The clusters bunch around the discrete allowed classical frequencies for the given actions $j_1, \ldots, j_N$.

In the classically choatic regions the Fourier spectrum X_ω fills in, perhaps completely. No finite set of fundamentals can conspire to yield all the complexity in the spectrum, and indeed no set of actions is constant

during the dynamics of a single trajectory. In a sense, the trajectory is able to sample all the frequencies now, since the actions are not conserved, thus the filling in of the Fourier spectrum X_ω. We now conclude with a few arguments to show that X^Q_ω has qualitatively the same behavior, namely many more "lines" in the spectrum, and approaching the classical continuum spectrum as $\hbar \to 0$.

A wavepacket $|g\rangle$ placed in a choatic region of classical phase space still has a smooth energy envelope, but now far more "lines" appear under the envelope,[3] because the chaotic wavefunctions of appropriate energy all sample the vicinity of the wavepacket. Thus, many more f_n's are nonzero in the chaotic region, compared to a similar wavepacket of in a quasiperiodic domain, for the same number of degrees of freedom.[3] Furthermore, since the eigenstates $|n\rangle$ in the chaotic region are globally distributed, the matrix element $X_{nn'}$ will follow a random-like distribution as a function of n and n; and the energies $E_{n'}$ likewise will not be derivable from any regular spacing formula such as Eq. (15). Such a lack of systematic behavior in each of the quantities f_n, $X_{nn'}$ and $\Delta_{nn'}$ in Eq. (11) implies no separation into fundamental, overtones, etc. is possible. Indeed, for fixed $\hbar$, Eq (11) evidently gives a very wild and random filling in of what were the "empty" regions between the clusters. This is because there are many, many possible $\Delta_{nn'}$ values, and nothing to distinguish them from each other because f_n, X_{nn}, etc. refuse to follow a "pattern". The only systematic aspect of the spectrum X^Q is that it does cut off at large frequencies, since the f_n's have to fall of at large n, corresponding to the finite energy width of the wave packet $|g\rangle$.

We thus have the qualitative trends:

Quasiperiodic Regime: Many "missing" frequencies

Chaotic Regime:

Filling in of the spectrum, no systematically missing lines.

These statements are true for both X_ω and X^Q_ω. They are in exact accord with the spectral features of molecular electronic transition discussed in earlier work.[3] Indeed, a quantitative criterion for the extent of quantum chaos was constructed from the observation that missing lines correspond to quasiperiodic motion.[3]

In this paper, we have examined the correspondence between X_ω and X^Q_ω, using a displaced, initially localized a wavepacket to determine X^Q_t as an expectation value. We have found certain similarities and differences between X_ω and X^Q_ω. Earlier, Marcus and co-workers[4] had examined the Fourier spectrum of a single (but specially selected) classical trajectory and associated it directly with one and two quantum transitions in a vibrating molecule. This idea has it roots in the earliest days of quantum mechanics, when it was noticed that classical frequencies correspond to quantum energy level spacings (Bohr Correspondence Rule) (see Eqn. (14)). Using this idea, one is able to get intensities and frequencies of transition between states of similar quantum numbers[4] (i.e. large quantum jumps cannot be gotten so well with classical mechanics, unless $\hbar \to 0$). In any case, the viewpoint of Refs. (4) is complementary to our own, in that we have used wavepackets to create an X^Q_t, and in so doing we rely on Ehrenfests' theorem for an $\hbar \to 0$ correspondence. Marcus and co-workers[4] have on the other hand relied more heavily upon the Bohr correspondence rule (Eq. (14)). Both approaches provide insight into the relationship between classical and quantum mechanics.

APPENDIX

A semiclassical, WKB wavefunction in one dimension is of the form

$$\psi_n^{WKB}(x) = \frac{1}{\sqrt{p_n(x)}} e^{i/\hbar \int^x p_n(x')dx'} \tag{A1}$$

where $p_n(x)$ is the momentum at position x of a classical particle of energy E_n. The matrix element $X_{nn'}$ reads

$$X_{nn'} = \int \psi_n^*(x) \, X \, \psi_{n'}(x)dx \tag{A2}$$

$$= \int dx \, \frac{e^{-i/\hbar \int^x p_n(x')dx' + i/\hbar \int^x p_{n'}(x')dx'}}{\sqrt{p_n(x) \, p_{n'}(x)}} \, X$$

We now make the approximation

$$p_n(x') - p_{n'}(x') = \frac{\partial p}{\partial n}\bigg|_{\bar{j}} (n-n') = \frac{\partial p}{\partial j}\bigg|_{\bar{j}} h(n-n') \tag{A3}$$

where

$$\bar{j} = \left(\frac{n+n'}{2} + \frac{1}{2}\right) h$$

Next, we note that

$$\frac{\partial p}{\partial j}\bigg|_{j=\bar{j}} = \frac{m}{\bar{p}} \frac{\partial E}{\partial j}\bigg|_{j=\bar{j}} = \frac{m\bar{v}}{\bar{p}} \tag{A4}$$

The integral in the exponent of (A3) now reads

$$-\frac{i}{\hbar}(n-n')h \int^x \frac{m\bar{v}}{\bar{p}(x)} dx = -\frac{i}{\hbar}(n-n')h\bar{v} \int^t dt'$$

$$= i \Delta_{nn',t} \tag{A5}$$

Then if we approximate $\sqrt{p_n(x)p_{n'}(x)}$ by $\bar{p}(x)$

we have

$$X_{nn'} \sim \int e^{i\Delta_{nn'}t'} X_{t'}dt' \quad , \tag{A6}$$

the desired result.

References

1. See, for example, K. Gottfried, Quantum Mechanics (Benjamin, New York, 1966).

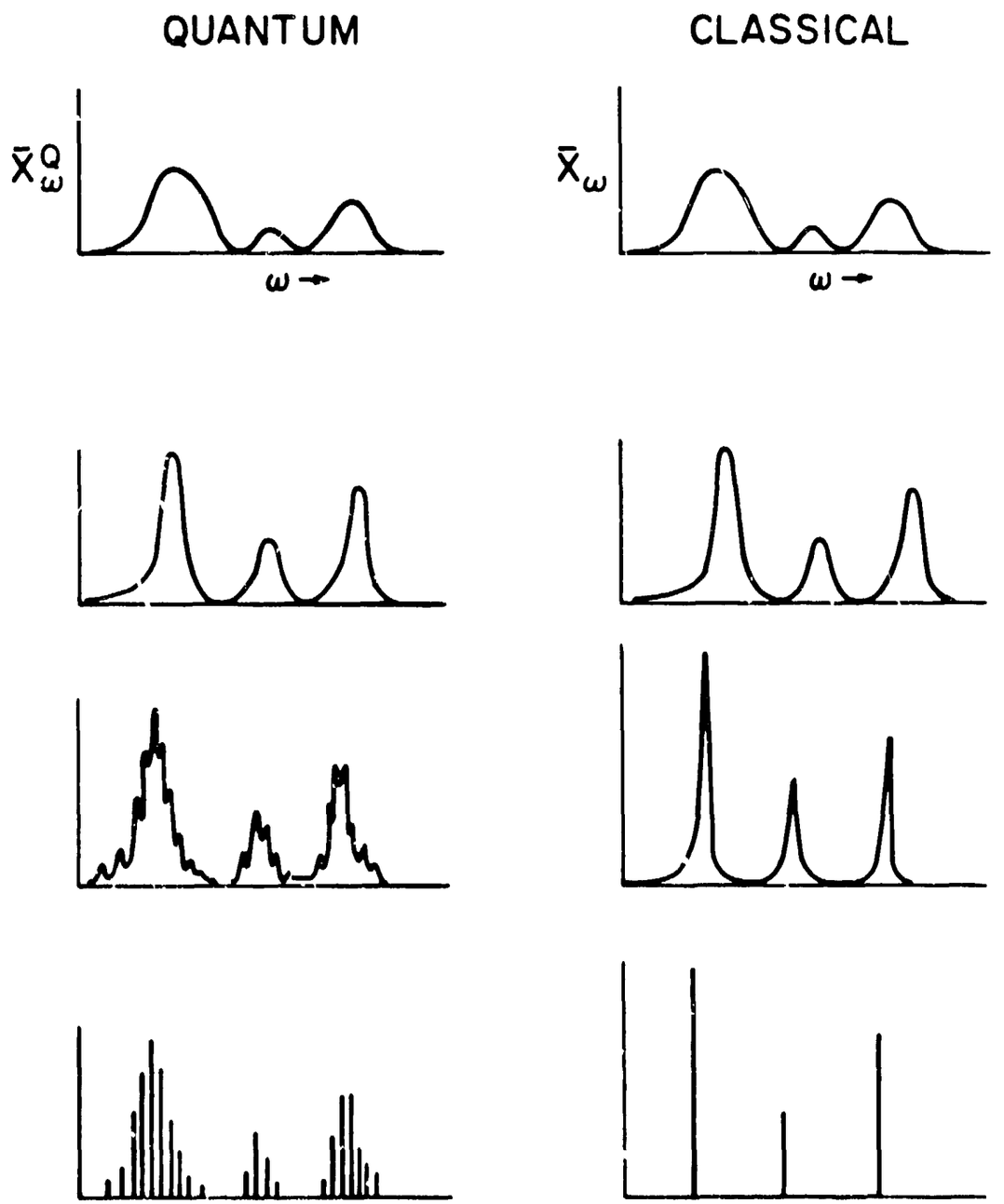
2. See, for example, W. H. Louisell, Quantum Statistical Properties of Radiation (Wiley, New York, 1973).

3. E. J. Heller, J. Chem. Phys. 72, 1337(1979); M. J. Davis, E. B. Stechel, and E. J. Heller, Chem. Phys. Lett. 76, 21(1980).

4. D. W. Noid, M. L. Koszykowski, and R. A. Marcus, J. Chem. Phys. 67, 404(1977), M. L. Koszykowski, D. W. Noid, and R. A. Marcus, J. Chem. Phys. 86, 2113(1982) and reference therein.

Figure Captions

1. In the left column we see the quantum spectrum and in the right, the classical, at increasing resolution as we move down the column. The classical and quantum spectra agree until the third case from the top. After that, the differences persist, showing the quantum spectrum to have band structure not present in the classical spectrum. This is the case in the classically quasiperiodic region.


QUANTUM
CLASSICAL
$\bar{X}^{Q}_{\omega}$
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