Quantization of non-integrable Hamiltonian by periodic orbits: a case study of chaotic DCN vibration

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Abstract

The action integrals of periodic orbits of the non-integrable (chaotic) two-mode system of DCN stretch vibration were analyzed to show ample linear relations. This enables us to obtain by extrapolation all the action integrals of any periodic orbits and at any energies from very few arbitrary action integrals. Based on this property, a very simple and easy semiclassical quantization algorithm by numerical arithmetic was proposed for low excitation which is chaotic classically. The result shows less than 1% deviation from the exact quantal method.

1. Introduction

Bohr’s idea of the standing wave of electron circulating around the nucleus was extended by Sommerfeld [1] that for a Hamiltonian system in which the coordinates are cyclic variables, the integral of each canonical momentum with respect to its coordinate over a cycle of its motion, called the action integral, must be an integral multiple of the Planck constant. Later, the EBK (Einstein, Brillouin and Keller) quantization condition [2] for integrable systems was given with the introduction of Maslov index for more general situations. For a nonintegrable system which is generally chaotic, the breakdown of periodic orbits hinders the application of Bohr–Sommerfeld or EBK quantization method. The quantization of a non-integral (or chaotic) system has been a historic issue since it is related to the very essence of the correspondence between classical and quantum motion. In this aspect, we have to take notice of Gutzwiller’s trace formula which expresses the quantum density of states in the semiclassical limit as a sum over isolated periodic orbits [3]. According to KAM (Kolmogorov, Arnold, Moser) theorem, the destruction of periodic orbits in the nonintegrable system is a gradual process that as the perturbation on the integrable part is increased, there is the energy range where the chaotic and periodic orbits coexist [3,4]. This corresponds to the lowly excited realm. Hence, there still exists the possibility that we can employ the traditional action integral method for the lowly excited system by the remnant periodic
orbits to explore the quantization condition for a nonintegrable (and chaotic) system. This is the goal of this study. In the following, the chaotic vibration of DCN will be employed for the case study. First, the action integrals of the periodic orbits of various periods embedded in the chaotic ‘sea’ will be presented to show their linear relationships. Then an algorithm based on these action integrals will be given for the semiclassical quantization of lowly excited vibration. The linear relations of the action integrals for various periodic orbits as a function of state energy are of particular interest since they will lead to the elucidation of quantized levels simply from the arbitrarily chosen system energies.

2. The chaotic vibrational dynamics of DCN

The vibrational dynamics of DCN we consider is composed of two bonds: D–C and C–N. The vibrational frequencies of these two bonds are roughly 2680 and 1950 cm\(^{-1}\), respectively. Since the frequency ratio is 1.3, the resonance can be 1:1 and 2:3. Together with the Morse model, an algebraic Hamiltonian can be written down for this coupled two-mode system as

\[
H = \omega_s \left( n_s + \frac{1}{2} \right) + \omega_t \left( n_t + \frac{1}{2} \right) + X_{st} \left( n_s + \frac{1}{2} \right)^2 + X_{nt} \left( n_t + \frac{1}{2} \right)^2 + X_{st} \left( n_s + \frac{1}{2} \right) \left( n_t + \frac{1}{2} \right) + K_s (a_s^+ a_s + \text{h.c.}) + K (a_t^+ a_t + \text{h.c.,})
\]

where \(s\) and \(t\) subscripts denote the D–C and C–N stretch coordinates, respectively. \(\omega\) and \(X\) are the frequency and nonlinear parameters. \(n\) is the action. \(K_s\) and \(K\) are the 1:1 and 2:3 coupling strengths. \(a\) and \(a^+\) are the destruction and creation operators. The coefficients can be determined by the fit of the eigenenergies of the energy matrix constructed from the algebraic Hamiltonian with the bases, \(|n_s, n_t\rangle\) \((n_s, n_t = 0, 1, 2, \ldots)\) to the experimental data. This was done as reported in [5]. The results (in cm\(^{-1}\)) are:

\[
\omega_s = 2681.4, \quad \omega_t = 1948.9, \quad X_{st} = -21.2, \quad X_{nt} = -0.3, \quad X_{st} = -34.3, \quad K_s = -88.7, \quad K = 13.8.
\]

This system is nonintegrable and chaotic. Except energy, there are no constants of motion. For a semiclassical study, we may cast \(a\) and \(a^+\) via Heisenberg correspondence [6]

\[
a_s^+ \rightarrow \sqrt{n_s} e^{i \phi_s}, \quad a_s \rightarrow \sqrt{n_s} e^{-i \phi_s}
\]

and employ the generalized coordinates \(q, p\) as [7]

\[
q_s = \sqrt{2n_s} \cos \phi_s, \quad p_s = -\sqrt{2n_s} \sin \phi_s \quad (x = s, t).
\]

In this way, we have the system Hamiltonian expressed in terms of \((q_s, p_s, q_t, p_t)\) coordinates. The equations of motion [7] are

\[
\frac{\partial H(q_s, p_s, q_t, p_t)}{\partial q_s} = -\frac{dp_s}{dt}, \quad \frac{\partial H(q_s, p_s, q_t, p_t)}{\partial p_s} = \frac{dq_s}{dt} \quad (x = s, t).
\]

Up to this point, we have succeeded in constructing a dynamical phase space in the \((q_s, p_s, q_t, p_t)\) space. The phase space corresponding to an eigenstate can be obtained from the solutions to the equation \(E = H(q_s, p_s, q_t, p_t)\) with \(E\) the eigenenergy. From each \((q_s, p_s, q_t, p_t)\) of the solution (phase) space, an orbit can be traced out via the integration of the equations of motion. Hence, there are numerous classical orbits corresponding to a quantal state. This is a classical interpretation. As a state is not of too high energy, besides periodic orbits, there are also initial point sensitive orbits which are chaotic. In other words, we interpret a state in the phase space as composed of orbits: some are periodic and the rest are chaotic. They are coexistent in the phase space. This has been the topic of our previous report [8].

We have calculated energy levels, and we have developed a simple algebraic algorithm which connects each quantum eigenvalue with periodic orbits having integer values of the classical action.

3. Action integrals of periodic orbits

3.1. Periodic orbits

Periodic orbits in a phase space can be viewed via the Poincare surface of section: either on \((q_s, p_s)\) with \(q_s = 0\) and \(p_s < 0\) or on \((q_t, p_t)\) with
$q_s = 0$ and $p_t < 0$. For convenience and just conventionally, we define the period of a periodic orbit as the number of points left on these Poincare surfaces of section. For a periodic orbit, there are traces left on both $(q_s, p_t)$ and $(q_t, p_s)$ surfaces. We use the notation $p^n$ or $q^m$ to represent an orbit if viewed on $(q_s, p_t)$ surface of section it is of period $n$ and on $(q_t, p_s)$ surface it is of period $m$. So we have both $p^n$ and $q^m$ notations for a periodic orbit. (In this Letter, $n$ and $m$ are treated as variables of integers.) In general, $m$ is related to $n$ and they are not equal. For instance, for a $p^3$ orbit, we have $q^4$. For $p^5, p^7, p^8, p^9, p^{12}, p^{15}, p^{18}$ orbits, we have, respectively, $q^7, q^9, q^{11}, q^{12}, q^{16}, q^{20}$ and $q^{24}$. These periodic orbits were found by numerical search. The deviation of the paths of these orbits is generally around five parts in a million in a duration of 10 ps. So, the calculational accuracy is high enough. It is interesting to note that the plot of $m$ versus $n$ shows a linear relation. The slope $m/n$ is close to 1.313 which is very close to the frequency ratio of D–C and C–N. For a state with energy $E$ (which may not be an eigenstate under classical consideration) there are numerous orbits sharing a common $p^n$ (and of course $q^m$). The exception is $p^1$ for which we still have $q^1$ and there are but two distinct $p^1(q^1)$ orbits of which energy is highly localized on D–C and C–N stretches, respectively. Since the bond displacement phases of D–C and C–N stretches of these two period-1 orbits are antisymmetric and symmetric, we label them as $p^1_1(q^1_s)$ and $p^1_2(q^1_s)$, respectively. For visualization, the $p^1_1(q^1_s), p^1_2(q^1_s)$ and $p^3(q^4)$ orbits of levels 11 and 22 (Levels are numbered from the lowest one.) on $(q_s, p_t)$ and $(q_t, p_s)$ surfaces are shown in Fig. 1.

![Fig. 1](image_url)

Fig. 1. The orbits of $p^1(q^4)$ (level 22) and $p^1_1(q^1_s), p^1_2(q^1_s)$ (level 11) and on the $(q_s, p_t)$ and $(q_t, p_s)$ surfaces. ▲ and △ indicate the intersections of the orbits on the surfaces. ▲ shows $p_s$ or $p_t < 0$, △ shows $p_s$ or $p_t > 0$. Arrows show the direction of the orbits. See text for details.
3.2. Action integrals

For each periodic orbit, we define its action integral, \( L \), as
\[
L = \frac{1}{2\pi} \oint p \cdot dq = \frac{1}{2\pi} \left( \oint p \, dq_i + \oint p_i \, dq \right),
\]
where the integration is along one cycle of the orbit. For different periodic orbits sharing a common \( p^r \), their action integrals are found to be the same. Therefore, we can write \( L(p^r) \) (or \( L(q^m) \)). Similarly, we also have \( L(p^1) \) and \( L(p^1) \). Shown in Fig. 2 are the \( L \) values of various \( p^r \) we found as the function of energy, \( E \). The numbers on the E-axis show where the eigenlevels are. Though the data are far from complete, they are sufficient to demonstrate that:

1. For each \( p^r \) (and also \( p^1 \) and \( p^1 \)), \( L \) is linear with respect to \( E \). So is \( q^m \), against \( E \). (Note that \( E \) is treated as a continuous variable.)
2. For each \( E, L \) is linear with respect to \( n \) and \( m \). This is shown in Fig. 3 for level 17 as an example. Obviously, \( L(p^1) \) together with \( L(p^r) \) and \( L(p^1) \) with \( L(q^m) \) share the linear relation against period. More specifically, we have
\[
L(p^1) : L(p^1) \approx i : j,
\]
\[
L(q^m) : L(q^m) \approx s : t.
\]
3. For the low eigenstates and smaller \( n \), \( L(p^r) \) (also \( L(q^m) \)) are (or very close to) integers.

From Fig. 2, we have from the extrapolation that for the ground state,
\[
L(p^r) = L(p^1) = L(p^1) = 0.
\]

This means that there is but one fixed point in the phase space for the ground state, i.e., all its periodic orbits shrink to a point. So does its phase space.

These ample linear relations enable us to obtain all \( L(p^r) \) for any \( E \) from very few \( L \) values. For instance, if we know \( L(p^1), L(p^1) \), and \( L(p^3) \) at any two arbitrary energies \( E_1 \) and \( E_2 \), then from Fig. 2, all \( L(p^1), L(p^1) \), and \( L(p^3) \) at any energy can be known. For any \( E \), since \( L(p^1), L(p^1) \) are known, all its \( L(p^r) \) are then known (like that shown in Fig. 3). Furthermore, from the known \( L(p^1) \) and \( L(q^m)(= L(p^3)) \), all \( L(q^m) \) can be known, which are in fact equal to their corresponding \( L(p^r) \). We will see in the next section that this leads to a very simple and easy way of finding out the quantal levels of low excitation.

4. The search of quantal levels via \( L(p^1), L(p^1) \) and \( L(p^3) \) of integer values

When we compare the numerically computed quantum eigenvalues with the numerical values of the classical actions of the periodic orbits, we find an unexpected simple pattern. The action \( L(p^1) \) and either \( L(p^1) \) or \( L(p^3) \) are close to integers.
The definition of the DCN vibrational levels. Since
our numerical algorithm (shown below) up to
in finding out the periodic orbits. This will limit
the prevailing chaotic dynamics, there is difficulty
along orbit the energy eigenvalues by quantizing the actions
while
defines the
finer
p
15
000 cm
inverting this relationship and predict
the coarse resolution of around 1900–2500 cm
The inverted
relations are shown below with positive
n
3 (which are, in fact, \( L(p^3) \), \( L(p^1_a) \) and \( L(p^3) \)), respectively:

\[
\begin{align*}
e_1 \text{ (cm}^{-1} \text{)} &= 1919.1n_1 + 2304.4, \\
e_2 \text{ (cm}^{-1} \text{)} &= 2521.7n_2 + 2453.4, \\
e_3 \text{ (cm}^{-1} \text{)} &= 632.9n_3 + 2343.5.
\end{align*}
\]

These equations are obtained from the fit of
data in Fig. 2. Though it is found that an eigen-
state possesses integer \( n_1, n_2 \) or \( n_3 \), the converse
does not hold. This is especially true that integer \( n_3 \)
does not necessarily correspond to an eigenenergy.
In other words, \( n_3 \) is limited by \( n_1 \) and \( n_2 \). This can
be understood by the consideration that the period
of a periodic orbit defines inverse-proportionally
the resolution of the level spectrum. \( p^1 \) and \( p^3 \) offer
the coarse resolution of around 1900–2500 cm
while \( p^3 \) offers the resolution down to around
600 cm
. These resolutions are enough for the
definition of the DCN vibrational levels. Since \( p^3 \)
defines the
finer structure of the level spectrum by
\( p^1 \) and \( p^3 \), \( n_3 \) has to be limited by \( n_1 \) and \( n_2 \). In
other words, we have to choose \( n_3 \) integers to
obtain the levels lying in between those levels by
\( n_1 \) and \( n_2 \). Meanwhile, for too high levels, due to
the prevailing chaotic dynamics, there is difficulty
in finding out the periodic orbits. This will limit
our numerical algorithm (shown below) up to
15000 cm
. In summary, it is found that the
quantal levels can be reconstructed by the follow-
ing steps:

(i) With \( n_1 = 0, 1, 2, \ldots \), we have levels as shown
in column (a) of Fig. 4.

(ii) With \( n_2 = 1, 2, \ldots \), we have levels as shown in
column (b) of Fig. 4. \( n_2 = 0 \) defines the level
very close to that by \( n_1 = 0. \)

(iii) In between those levels in column (a) and (b)
with \( n_1 = n_2 \equiv n_0 \) (connected by the dashed
lines), there are the levels with energies \( e_3 \) of
which \( n_3 = 3n_0 + 1, 3n_0 + 2, \ldots, 4n_0 - 1. \) This
is shown in column (c). (It needs mention that
a level is defined by \( n_1, n_2 \) or \( n_3 \), not by \( n_1, n_2 \)
or whatever.) Column (d) shows the recon-
structed levels. Indeed, the levels by this
\textit{classical} numerical algorithm are very close to the
quantal levels which are shown in column (e).
Shown in Table 1 are the eigenenergies by this
algorithm and the quantal values. The devia-
tions are not larger than 100 cm
, i.e., the
errors are less than 1%.

By this observation and analysis, therefore, we
may propose a quantization process: it starts from
choosing \textit{any two arbitrary} energies (which are most
possibly not the eigenenergies), finding out their
corresponding \( p^3, p^1, p^a \) orbits (among the chaotic
sea) from the solutions to the equation \( E = H(q, \dot{q}, \dot{p}) \)
(assuming that its coefficients are known)
and the equations of motion, calculating their
action integrals and following the method mentioned
in the last section to obtain \( L(p^1), L(p^a) \) and \( L(p^3) \) as
the functions of energy. Then by the previous fitted
linear equations and the reconstruction steps, the quantized levels can be drawn down.

Resonances 1:1 and 2:3 of DCN, individually, will conserve $n_1 + n_2$ and $n_1/2 + n_2/3$, respectively. However, their simultaneous emerging will break the conservation. The breakdown is not so serious that both these actions are approximate constants of motion [5]. It is interesting to note that $n_1$ and $n_2$ for those levels shown in columns (a) and (b) of Fig. 4 are the approximate constants of motion: $n_1 + n_2$. This sheds hint on the connection between $L(p^1)$ and the constants or approximate constants of motion. Our preliminary study of the Henon–Heiles Hamiltonian [9] also confirms this speculation that $L(p^1)$ and $L(p^2)$ of the liberating (L) and processing (P) period-1 orbits play special connection with the total action, which is the constant of motion, of the system. Their exact relations are believed to be of fundamental importance and need further exploration.

### 5. Concluding remarks

The application of Bohr–Sommerfeld or EBK quantization to nonintegrable system has been of doubt due to the occurrence of chaos. This was originally pointed out by Einstein. Our case study shows that, at least for low excitation, the situation is not so pessimistic. The remnant periodic orbits in the sea of chaotic orbits inherit the properties that are related to the quantization. Indeed periodic orbits, though scarce in a chaotic system, form the invariant skeleton of the phase space and possess important characters relating to the (approximate) constants of motion and the quantal levels. This observation suggests a classical numerical algorithm for the quantization as demonstrated in this DCN case. Though the vibrational case of DCN was employed numerically, it is expected that this algorithm can be generic if one notices that the coefficients of the nonlinear Hamiltonian as shown in Section 2 bear little

### Table 1

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<th>By $p^1_a$</th>
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The quantal levels are also shown for comparison. See Fig. 4 and text for details.
influence on the results. On the other hand, we have reported that the criterion of least global chaoticity throughout the whole phase space via the chaotic orbits can also lead to proper quantization [10] for the nonintegrable system. These works shed on the speculation of intrinsic connection between periodic and chaotic orbits in a nonintegrable system. Though KAM theorem shows the evolution of the periodic and chaotic orbits, much unknown still remains for further exploration.

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References