Torus Quantization in LocalMode Region for Two Kinetically Coupled Morse Oscillators

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Abstract This paper reports the method and the results of the torus quantization in local mode region for a system of two kinetically coupled Morse oscillators. It is found that the semiclassical result agrees very well with the quantum result as the quantizing torus is far from resonance and local-normal separatrix.

Key words EBK quantization condition; quantizing torus; local mode

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两运动耦合的 Morse振子系统局域模区域内环量子化

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[摘要] 报导了两运动耦合的 Morse振子系统局域模区域内环量子化的方法和结果. 发现当量子化环远离谐振带及局域-本征分界线 (Local-Normal Separatrix)时, 半经典量子化的结果与量子力学的结果符合得很好.

[关键词] EBK量子化条件, 量子化环, 局域模

0 Introduction

The stretch motions of a symmetric triatomic molecular system with small mass ratio, between the light atom and the heavy central atom, can be well approximated by two kinetically coupled Morse oscillators with the following Hamiltonian

$$H = \frac{\tilde{p}_1^2}{2m} + D(1 - e^{-\beta\tilde{x}_1})^2 + \frac{\tilde{p}_2^2}{2m} + D(1 - e^{-\beta\tilde{x}_2})^2 + \alpha\tilde{p}_1\tilde{p}_2, \tag{1}$$

which can be scaled into the following form

$$\varepsilon = \frac{p_1^2}{2} + (1 - e^{-x_1})^2 + \frac{p_2^2}{2} + (1 - e^{-x_2})^2 + \delta p_1 p_2, \tag{2}$$

by the transformations

$$\varepsilon = \frac{H}{D}, \quad p_i = \frac{1}{\sqrt{mD}}\tilde{p}_i, \quad x_i = \beta\tilde{x}_i, \quad \tau = D\gamma t,$$

where $\delta = m\alpha = \frac{m}{M}\cos\theta$ is the coupling constant that relates the finite mass M of the central atom. m is the reduced mass of the light atom and the heavy central atom. θ is the angle made by the two bonds of the molecule.

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D is the dissociation energy of a Morse oscillator, β is Morse parameter of the system, $\gamma = \omega_0/\sqrt{2D}$ is a system dependent constant with $\omega_0 = \sqrt{2\beta^2 D/m}$ being the small oscillation frequency of the Morse oscillator. For small coupling parameter δ, phase space can be classified into local mode and normal mode regions. Classical motions in phase space can be tori (regular motion), periodic orbits, and chaotic trajectories (irregular motion). As δ becomes bigger, the area of resonances will grow by eating up more and more local mode tori. This system was first studied with simplifications by Jaffé and Brumer[1], and then by Sibert III, Hynes and Reinhardt[2], classically. Recently, we studied this system by constructing semiclassical wave functions for quantizing torus for uncoupled system torus[3], coupled system torus[4] in regular region and cantorus[5] in chaotic region. At higher energy and strong coupling, this system has many strong resonances in phase space, to completely determine the correspondence between quantum states and phase space structures, one needs to do semiclassical quantization numerically.

This paper reports in detail the method and the results of semiclassical quantization for energy eigenvalue for tori in local mode region for a system of two kinetically coupled Morse oscillators.

1 Torus Quantization in Regular Local Mode Region

1.1 The EBK quantization conditions

If a torus corresponds to a quantum state, then it satisfies the EBK quantization conditions

$$I_1 = \frac{1}{2\pi}\oint_{C_1}(p_1\,dx_1 + p_2\,dx_2) = \hbar\gamma\left(n_1 + \frac{1}{2}\right), \tag{3}$$

$$I_2 = \frac{1}{2\pi}\oint_{C_2}(p_1\,dx_1 + p_2\,dx_2) = \hbar\gamma\left(n_2 + \frac{1}{2}\right), \tag{4}$$

where C_1 and C_2 are two topologically independent circuits around the torus in phase space. γ is system dependent constant, for the two kinetically coupled Morse oscillators, it is given by $\gamma = \omega_0/\sqrt{2D}$.

1.2 The method of torus quantization in local mode region

To completely specify a trajectory in phase space, one usually needs four variables, which can be taken as the coordinates and momenta of a trajectory. It is necessary to have three independent variables to specify a torus for an energy conservative system. The number of independent variables can be further reduced by inspecting the phase space structures because a torus consists of infinite number of trajectories. SOS provides a good way to identify a torus, especially the local mode torus of this two kinetically coupled Morse oscillators system, since in a SOS at $x_1 = 0$, $p_1 > 0$, all the local mode tori have intersection point on the line $x_2 = 0$. So, if one starts to search local mode torus along the line of $x_2 = 0$ in the SOS at $x_1 = 0$, $p_1 > 0$, the remaining independent variable is p_2 for a given energy ε. To find a quantizing torus, one needs to change system energy ε, so that a quantizing torus exists in that energy. This energy is called semiclassical energy of the system. Therefore, one needs two independent variables to specify a quantizing torus, which can be chosen as (p_1, p_2) or (ε, p_1) or (ε, p_2).

The circuits C_1 and C_2 in equations (3~4) are taken to be the intersections of the torus with SOS at $x_2 = 0$, $p_2 > 0$ and SOS at $x_1 = 0$, $p_1 > 0$. The quantization conditions become

$$I_1(\varepsilon, f) = \frac{1}{2\pi}\oint_{C_1} p_1\,dx_1 = \left(n_1 + \frac{1}{2}\right)\gamma\hbar, \tag{5}$$

$$I_2(\varepsilon, f) = \frac{1}{2\pi}\oint_{C_2} p_2\,dx_2 = \left(n_2 + \frac{1}{2}\right)\gamma\hbar, \tag{6}$$

where f is a function of p_1 or p_2 of the quantizing torus, and ε is the semiclassical eigenenergy corresponding to this torus.

Since each action is a function of system energy ε and the parameter f of the torus in phase space, searching a quantized torus is to search a torus in phase space by varying ε and f so that the quantization conditions (5) and (6) are satisfied simultaneously. Numerically, this is to first set a guessed energy ε^* and a guessed parameter f^*

of the torus in phase-space, and then to use Newton-Raphson method to converge to the true eigenenergy and the true quantizing torus. According to Newton-Raphson algorithm, the first correction to the guessed energy ε^* and the guessed parameter f^* of the torus is given by the solution of the following linear equations

$$\begin{pmatrix} \dfrac{\partial I_1(\varepsilon^*, f^*)}{\partial \varepsilon} & \dfrac{\partial I_1(\varepsilon^*, f^*)}{\partial f} \\ \dfrac{\partial I_2(\varepsilon^*, f^*)}{\partial \varepsilon} & \dfrac{\partial I_2(\varepsilon^*, f^*)}{\partial f} \end{pmatrix} \begin{pmatrix} \Delta\varepsilon \\ \Delta f \end{pmatrix} = - \begin{pmatrix} I_1(\varepsilon^*, f^*) - \left(n_1 + \dfrac{1}{2}\right)\hbar\gamma \\ I_2(\varepsilon^*, f^*) - \left(n_2 + \dfrac{1}{2}\right)\hbar\gamma \end{pmatrix}, \tag{7}$$

and the new energy and the new parameter of the torus are given by

$$\varepsilon^* \leftarrow \varepsilon^* + \Delta\varepsilon, \tag{8}$$

$$f^* \leftarrow f^* + \Delta f. \tag{9}$$

The second correction to the energy ε and the parameter f of the torus comes from the solution of the same linear equation (7) but with a new guessed energy and a new guessed parameter given by (8) and (9). This process will be repeated for many times until the required precision in the following

$$\mathrm{err}f = \left| I_1 - \left(n_1 + \frac{1}{2}\right)\gamma\hbar \right| + \left| I_2 - \left(n_2 + \frac{1}{2}\right)\gamma\hbar \right| < \delta_1 \tag{10}$$

or

$$\mathrm{err}x = |\varepsilon^* - \varepsilon| + |f^* - f| < \delta_2 \tag{11}$$

has been obtained. The partial differentiations in the matrix elements in equation (7) are calculated numerically by 3-point method. For a good precision one may use 5-point method, but it will use more CPU time.

1.3 The action calculation for local mode torus

The actions I_1 and I_2 correspond to areas enclosed by the closed circuits C_1 and C_2 made by the intersections of a trajectory with SOS at $x_2 = 0$, $p_2 > 0$ and SOS at $x_1 = 0$, $p_1 > 0$ respectively. To numerically calculate the area we start from Lagrange polynomial interpolation formula[6]

$$\int_a^b g(x)\,\mathrm{d}x \approx \int_a^b P_n(x)\,\mathrm{d}x = \int_a^b \sum_{k=0}^{n} \frac{\tilde{\omega}}{(x - x_k)\tilde{\omega}'(x_k)} g(x_k)\,\mathrm{d}x, \tag{12}$$

where

$$\tilde{\omega}(x) = (x - x_0)(x - x_1)\cdots(x - x_n)$$

$$\tilde{\omega}'(x_k) = (x_k - x_0)(x_k - x_1)\cdots(x_k - x_{k-1})(x_k - x_{k+1})\cdots(x_k - x_n).$$

$P_n(x)$ is a n^{th} order Lagrange polynomial; a, b are integration limits; and usually $(b-a)$ is very small to keep the numerical value calculated approximately at the right hand side of (12) closer to the exact integral at the left hand side of (12). For $n = 2$, $P_n(x)$ can be written as the following

$$\begin{aligned} P_2(x) &= \sum_{k=0}^{2} \frac{\tilde{\omega}(x)}{(x - x_k)\tilde{\omega}'(x_k)} g(x_k) \\ &= \frac{(x - x_1)(x - x_2)}{(x_0 - x_1)(x_0 - x_2)} g(x_0) + \frac{(x - x_0)(x - x_2)}{(x_1 - x_0)(x_1 - x_2)} g(x_1) + \frac{(x - x_0)(x - x_1)}{(x_2 - x_0)(x_2 - x_1)} g(x_2), \end{aligned}$$

and the result of the integral in (12) is

$$\begin{aligned} \int_{x_0}^{x} P_2(x)\,\mathrm{d}x = {} & \frac{g(x_0)}{(x_0 - x_1)(x_0 - x_2)} \left[\frac{(x_2^3 - x_0^3)}{3} - \frac{(x_1 + x_2)(x_2^2 - x_0^2)}{2} + x_1 x_2 (x_2 - x_0) \right] \\ & + \frac{g(x_1)}{(x_1 - x_0)(x_1 - x_2)} \left[\frac{(x_2^3 - x_0^3)}{3} - \frac{(x_0 + x_2)(x_2^2 - x_0^2)}{2} + x_0 x_2 (x_2 - x_0) \right] \\ & + \frac{g(x_2)}{(x_2 - x_0)(x_2 - x_1)} \left[\frac{(x_2^3 - x_0^3)}{3} - \frac{(x_0 + x_1)(x_2^2 - x_0^2)}{2} + x_0 x_1 (x_2 - x_0) \right], \end{aligned} \tag{13}$$

where x_0 and x_2 are the two nearest neighbors of x_1, then the total area of the closed curve is the sum of all small areas like the one given in (13) with the care of directions of the line integrals in (5) and (6).

The errors introduced by the polynomial approximation to the unknown function $g(x)$ can be analysized fur-

ther from the residue error function. As an approximate estimate, one can take the case of equal step size, the residue (or truncation) error function is given by

$$\mathrm{Res}[g] = \int_a^b g(x)\,\mathrm{d}x - \int_a^b P_n(x)\,\mathrm{d}x = \int_a^b \frac{g^{(n+1)}(\zeta)}{(n+1)!}\tilde{\omega}(x)\,\mathrm{d}x.$$

For $n = 2$

$$\mathrm{Res}[g] = -\frac{(b-a)^5}{2\,880}g^{(4)}(\eta), \quad \text{for } a < \eta < b.$$

Suppose $g^{(4)}(x)$ does not change very much in $[a, b]$, then the improved integral value is given by

$$I = I_{2N} + \frac{1}{2^5 - 1}(I_{2N} - I_N),$$

where I_{2N} and I_N are integral values gotten by partitioning the interval $[a, b]$ into $2N$ equal parts and N equal parts. So the error is about $(I_{2N} - I_N)$, if it is very small one will say that the calculation is accurate enough.

1.4 The consideration on the initial input to the search program

Since the convergence of Newton's method is strongly depending on how close are the guessed energy and the guessed parameter of the torus to the true eigenenergy and the parameter of the quantizing torus, a reasonable initial input to the search program is very important. This search program searches an initial action vector which is quantized according to (5) and (6). For weak coupling system, a zeroth order energy corresponding to the action vector to be searched should be a good choice, because the deformation from the zeroth order torus is very small. Searching a quantized torus of strongly coupled system is usually slow as the quantized torus of weak coupling system has to be found first and as an input to the search program of strongly coupled system. According to the analysis given in section 1.2, one can chose independent variables (ε, p_1) or (ε, p_2). Once the energy of the system has been chosen, the parameter f of the torus can be determined from the full Hamiltonian of the system. In the search following I chose f another way to represent p_1 to be the ratio of kinetic energy of the first Morse oscillator to the total energy of the system, i.e.

$$f = \frac{p_1^2}{2\varepsilon}, \tag{14}$$

which is related to the position of the torus with the aid of SOS at $x_1 = 0$, $p_1 > 0$. The initial inputs to the search program then are

$$x_1 = 0, \tag{15}$$

$$x_2 = 0, \tag{16}$$

$$p_1 = \sqrt{2f\varepsilon}, \tag{17}$$

$$p_2 = -\delta p_1 + \sqrt{2\varepsilon - (1-\delta^2)p_1^2}, \tag{18}$$

where

$$\varepsilon = \frac{2}{\lambda}\left[\left(n_1 + \frac{1}{2}\right) - \frac{1}{2\lambda}\left(n_1 + \frac{1}{2}\right)^2 + \left(n_2 + \frac{1}{2}\right) - \frac{1}{2\lambda}\left(n_2 + \frac{1}{2}\right)^2\right],$$

$$f = \frac{\frac{2}{\lambda}\left[\left(n_1 + \frac{1}{2}\right) - \frac{1}{2\lambda}\left(n_1 + \frac{1}{2}\right)^2\right]}{\varepsilon},$$

$$\lambda = \frac{2D}{\hbar\omega_0},$$

ε is the zeroth order energy for the system. I choose here the momentum maxima as the set of inputs to the search program. One could also choose turning points of the two Morse oscillators as an alternative input, it shows that the final results are same for both methods of input.

Note that the initial input (15) ~ (18) always gives local mode torus as energy and the parameter of the torus change a little bit because each of the local mode trajectories has an intersection point with line $x_2 = 0$ in the SOS at $x_1 = 0$, $p_1 > 0$.

1.5 Result and discussion of torus quantization in the regular local mode region

In this subsection we will show semiclassical results of two kinetically coupled Morse oscillators with coupling parameters $\delta = -0.014$ in Table 1. Other parameters used in the semiclassical calculation and quantum calculation are given by

$$D = 8.84 \times 10^{-19}\ \mathrm{J} = 44\,505.216\ \mathrm{cm}^{-1},$$
$$\beta = 2.175 \times 10^{8}\ \mathrm{cm}^{-1},$$
$$\omega_0 = 7.291\,6 \times 10^{14}\ \mathrm{s}^{-1}.$$

Table 1 The semiclassical results in local mode region for two kinetically coupled morse oscillators at $\delta = -0.014$

(n_1, n_2)	ε_s	err$f$	err$x$	dn_1	dn_2	$\bar{\varepsilon}_q$	$\lvert\varepsilon_s - \bar{\varepsilon}_q\rvert$
(1, 0)	0.169 00	0.1E-05	0.8E-05	0.3E-05	0.8E-06	0.169 24	2.44E-04
(2, 0)	0.248 53	0.9E-06	0.4E-05	0.1E-05	0.1E-05	0.248 51	1.50E-05
(3, 0)	0.324 19	0.7E-06	0.1E-05	0.1E-05	0.1E-06	0.324 18	8.92E-06
(4, 0)	0.396 06	0.1E-04	0.6E-04	0.4E-04	0.6E-06	0.396 06	3.60E-06
(3, 1)	0.407 23	0.8E-06	0.5E-05	0.8E-06	0.1E-05	0.407 24	1.22E-05
(5, 0)	0.464 14	0.4E-05	0.6E-05	0.8E-05	0.2E-05	0.464 14	1.00E-06
(4, 1)	0.479 18	0.4E-06	0.1E-04	0.6E-06	0.5E-06	0.479 16	1.77E-05
(5, 1)	0.547 29	0.3E-04	0.7E-05	0.4E-05	0.4E-05	0.547 28	5.92E-06
(6, 0)	0.528 44	0.3E-06	0.1E-05	0.6E-06	0.7E-07	0.528 44	1.95E-07
(7, 0)	0.588 95	0.5E-05	0.2E-05	0.2E-04	0.2E-05	0.588 95	1.17E-06
(6, 1)	0.611 60	0.1E-05	0.3E-06	0.9E-05	0.3E-06	0.611 60	2.74E-06
(5, 2)*	0.626 57	0.4E-02	0.8E-03	0.8E-02	0.4E-02	0.626 57	5.18E-07
(8, 0)	0.645 67	0.9E-06	0.5E-06	0.2E-05	0.1E-06	0.645 68	2.58E-06
(7, 1)	0.672 12	0.6E-05	0.9E-06	0.8E-05	0.2E-04	0.672 12	7.23E-07
(6, 2)	0.690 95	0.1E-05	0.1E-04	0.2E-05	0.2E-05	0.690 94	1.01E-05
(5, 3)	0.701 76	0.5E-05	0.9E-08	0.4E-04	0.4E-05	0.702 05	2.94E-04
(7, 2)	0.751 49	0.2E-05	0.1E-05	0.1E-05	0.3E-05	0.751 49	1.17E-06
(6, 3)	0.766 44	0.4E-06	0.5E-05	0.2E-06	0.9E-06	0.766 41	3.03E-05
(10, 0)	0.747 75	0.1E-03	0.8E-06	0.3E-03	0.5E-05	0.747 79	4.14E-05
(9, 1)	0.781 78	0.5E-04	0.9E-05	0.3E-04	0.9E-05	0.781 78	2.22E-06
(8, 2)	0.808 22	0.3E-04	0.6E-04	0.4E-04	0.3E-04	0.808 23	6.99E-06
(7, 3)	0.827 05	0.2E-05	0.1E-04	0.3E-05	0.3E-05	0.827 03	1.46E-05
(10, 1)	0.830 91	0.6E-05	0.1E-04	0.1E-04	0.1E-05	0.830 88	3.47E-05
(9, 2)*	0.861 21	0.8E-01	0.2E-03	0.4E-01	0.7E-01	0.861 17	4.57E-05
(8, 3)	0.883 81	0.8E-06	0.4E-06	0.2E-05	0.4E-06	0.883 81	4.37E-06
(7, 4)	0.898 72	0.5E-05	0.1E-05	0.1E-05	0.1E-04	0.898 69	2.78E-05
(10, 2)	0.910 30	0.2E-05	0.1E-04	0.4E-05	0.5E-06	0.910 29	1.09E-05
(9, 3)*	0.936 75	0.1E-04	0.5E-05	0.2E-04	0.8E-05	0.936 77	1.53E-05
(8, 4)	0.955 55	0.1E-03	0.3E-05	0.2E-03	0.5E-03	0.955 56	1.38E-05
(10, 3)*	0.985 90	0.3E-02	0.8E-05	0.2E-02	0.5E-02	0.985 86	3.56E-05
(9, 4)	1.008 58	0.2E-03	0.5E-06	0.2E-04	0.2E-03	1.008 57	1.06E-05
(8, 5)	1.023 43	0.7E-04	0.1E-04	0.2E-04	0.1E-03	1.023 42	8.54E-06
(9, 5)*	1.076 34	0.1E-02	0.1E-03	0.3E-01	0.2E-01	1.076 53	1.96E-04
(10, 6)	1.189 95	0.6E-05	0.1E-04	0.2E-05	0.1E-04	1.189 93	1.49E-05

We also got semiclassical results calculated numerically for different coupling parameter δ, and the results are not reported here. In Table 1, ε_s is semiclassical eigenenergy found numerically which is the same for (n_1, n_2) and (n_2, n_1) states in the primitive semiclasssical quantization (5) and (6); err$f$ is the precision reached in the quantization; err$x$ is the precision reached in the search by Newton-Raphson method; dn_1 is the absolute value in the difference between the obtained quantum number which is not an integer exactly and the preset quantum number n_1; similarly for dn_2. $\bar{\varepsilon}_q$ is the average quantum energy of the local mode doublet, and $(\lvert\varepsilon_s - \bar{\varepsilon}_q\rvert)$ is the absolute difference between the semiclassical eigenenergy obtained by primitive semiclassical quantization and the average quantum energy of the local mode doublet which is the result of dynamical tunneling between local mode (n_1, n_2) and local mode (n_2, n_1). Under the basis set of two uncoupled Morse oscillators, the quantum eigenvalues were obtained by diagonalizing the Hamiltonian of two kinetically coupled Morse oscillators with

the parameters given above. Except for a few states, as shown in Table 1, the results of primitive semiclassical quantization are in excellent agreement with the true quantum results. Those states that do not agree with quantum results very well are very close to strong resonances or local-normal separatrix where the local mode semiclassical quantizations have probably failed. It should be pointed out that state (9, 3) and state (10, 3) are special in the sense that there are four quantum levels stacked together around each primitive quantum state. Because of this, the quantum states (wave functions) show strong chaos. The argument here is that it must exist another primitive semiclassical state which is very close to the primitive state found, and the interactions among these tori states give chaotic wave functions. The difference between state (9, 3) and state (10, 3) is that state (9, 3) can be easily quantized by EBK rule but not state (10, 3). This is because that state (9, 3) is far from strong resonances, so the EBK quantization conditions can be used. State (10, 3) is different, this state is very close to 9/14 resonance which is in turn very close to 2/3 resonance, and the phase space around the state (10, 3) is chaotic, it is very difficult to find this state by EBK quantization conditions. Another example is the state (5, 3) which is very close to local-normal separatrix, even though the quantization conditions (5) and (6) are satisfied quite well, the searched semiclassical eigenenergy still has a $\sim 13\ cm^{-1}$ difference from the true quantum eigenvalue. This is attributed to the nonseparability of the system around the local- normal separatrix. It has been noticed that some quantum states can not be quantized primitively by torus quantization because strong resonances in phase space destroyed the tori required to do primitive semiclasical quantization. For examples, all the states marked with* except the state (9, 3) in Table 1 can not be quantized by the regular EBK method, because the tori corresponding to these states have been destroyed. The corresponding classical objects of some of these states are cantori in phase space, which can be quantized by quantizing periodic orbit through BS-EBK rule[7].

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