

Quantization of the nonintegrable Hamiltonian by Lyapunov analysis

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The classical Hamiltonian for which the dynamics is represented by trajectories in a multidimensional phase (coset) space is quantized via Lyapunov analysis. A system of one electron in four sites and the vibration of H₂O with Fermi resonance is studied. The quantization condition is that the average Lyapunov exponents show local minima as a function of the classical energy. This means that it requests the least global chaoticity. This quantization algorithm leads to results consistent with those obtained by the quantal models.

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I. INTRODUCTION

The quantization of a classical system was introduced by Bohr and then extended by Sommerfeld [1]. This was 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 must be an integral multiple of the Planck constant. Then, the Einstein, Brillouin, and Keller quantization condition for integrable systems was given with the introduction of the Maslov index for more general situations [2]. However, a general rule for quantization of nonintegrable systems has not been obtained since the remaining of quantum mechanics. Today, we know that chaotic motion is embedded in the nonintegrability of a dynamical system and this is related to the quantization of chaotic dynamics [3]. Recently, an approach to this topic has been developing based on the periodic orbits which form the invariant skeleton of the phase space. Gutzwiller [3] has been successful in giving a trace formula which relates the quantum density of states in the semiclassical limit to a sum over isolated periodic orbits. However, there are fundamental difficulties associated with convergence of Gutzwiller's formula [4].

It is now known, as noted in the literature [5–8], that via the coset-represented algebraic Hamiltonian, a classical Hamiltonian can be obtained. This is a very convenient Hamiltonian by which much dynamical information of the motion of one electron in the system of multisites and the highly excited molecular vibration can be retrieved.

The algorithm to obtain the coset-represented Hamiltonian is via the employment of the representatives of the coset space formed by the associated Lie group and its subgroup [9,10]. This means that the dynamical motion is described in the coset space which possesses a geometrical structure. For instance, for the three-coupled vibrational modes of H₂O: the two stretches and one bend with 1:1 resonance between the two stretches and the Fermi resonance among the bend and the stretches, the Lie algebra is SU(3) and the coset space is the three-dimensional sphere S³ [11]. The motion of one electron in the system of four sites can be described by the SU(4) algebra and the coset space is S⁴

[8,12]. Furthermore, by choosing the appropriate coordinates which will be denoted as (q_i, p_i) of the coset space, Hamiltonian equations of motion can be written down in terms of these coordinates as

$$\partial H(q,p)/\partial p_i = dq_i/dt, \partial H(q,p)/\partial q_i = -dp_i/dt.$$

Here, q and p stand for (q_1, q_2, \dots) and (p_1, p_2, \dots) , respectively. q_i and p_i form a pair of conjugate variables. For the aforementioned motion of one electron in the four-site system, $i = 1, 2, 3$, the coset space is six dimensional. For the system of H₂O, $i = 1, 2$, i.e., the coset space is four dimensional. In summary, in this coset formulation, both the electronic motion and the vibrational motion are described by the trajectories in a multidimensional coset space. The coset space is the phase space for the dynamics. The dynamics are classical and nonlinear. Therefore, many ideas in the nonlinear field [13] such as localization, fractal, chaos, and the Lyapunov exponent [14] can find their places in this analysis.

Albeit fruitful information can be drawn from the coset-represented $H(q,p)$ for our systems of electronic motion and molecular vibration, one serious drawback is that it cannot offer the quantized energy levels since the framework is classical. Our systems of electronic motion and molecular vibration are nonintegrable. It is the intention of this paper that via the analysis of the Lyapunov exponent, quantized levels can be resolved. One point that needs emphasis in our Lyapunov analysis is that for the elucidation of quantized levels, quantization is through the minimization of the average Lyapunov exponent which is obtained from randomly sampled trajectories in the phase space. What we require is the global minimization of chaoticity. This is different from Gutzwiller's idea based on periodic orbits, although unstable periodic orbits can possess nonzero Lyapunov exponents.

Before reaching the central topic, a brief introduction to the Lyapunov exponent is necessary. This is shown in the next section.

II. LYAPUNOV EXPONENT

The Lyapunov exponent [14] is defined as the average exponential rate of divergence of two nearby trajectories. It is an important parameter which characterizes the chaoticity of a trajectory and, hence, the system. For a chaotic system,

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FIG. 1. Three structures for the four-site model. They are labeled as $S1$, $S2$, and $S3$, respectively. The numbers designate the sites.

initially, the separation may be too small for one to distinguish two nearby points, i.e., the resolution is not high enough. As time elapses, the separation will grow, and finally, one may be able to tell the difference. In other words, information is being created. This is connected with a famous relation that states the sum of the positive Lyapunov exponents is equal to the entropy (the so-called Kolmogorov entropy) for a closed system [15]. The Lyapunov exponent, therefore, describes the essence of a chaotic system.

The number of the Lyapunov exponents equals the dimensionality of the space where the trajectory resides. However, for a Hamiltonian system, the Lyapunov exponents show up in pairs. For the system of one electron in four sites, the phase space is six dimensional. Conservation of energy reduces the dimension of the trajectories to five and only two exponents are independent. Fortunately, for these two exponents, one is much larger (up to 10^2 – 10^3 order) and only the larger one needs our calculation. Likewise, for the H_2O vibrational system, the phase space is four dimensional and only one exponent is independent. The algorithm for calculating the maximal Lyapunov exponent will be adopted in the following analysis. Its details have been shown in our previous reports and will not be reviewed here for brevity [16–18].

III. QUANTIZATION OF THE SYSTEM OF ONE ELECTRON IN FOUR SITES

A. Coset-represented Hamiltonian of one electron in four sites

Three structures of four sites [12] will be considered as shown in Fig. 1. They are labeled as $S1$, $S2$, and $S3$, for convenience.

The Hamiltonian analogous to the Huckel molecular orbital model (HMO) [19] can be written algebraically as

$$\sum e_i a_i^+ a_i + 1/2 \sum V_{kl} a_k^+ a_l$$

with e_i the energy at the i th site (atomic orbital) and $V_{kl}/2$ is the interaction between the k and l sites. e_i and $V_{kl}/2$ correspond to α and β values in HMO. a_i and a_i^+ are the destruction and creation operators. (For convenience, sites are labeled as 0 to 3.)

For this system, the coset representatives Ω are

$$N^{-1/2} \left(1 + \sum_{j=1,2,3} \tau_{j0} a_j^+ a_0 \right) |1000\rangle.$$

Here, $|1000\rangle$ represents the reference state that there is one electron on the zeroth site and none in the rest sites. τ_{j0} is the complex number. N can be elucidated by the normalization of Ω . N is obtained as

$$1 + \sum |\tau_{j0}|^2.$$

It is noteable that $\{\Omega\}$ is overcomplete. In other words, we can represent the *algebraic* Hamiltonian in terms of Ω in a diagonal form. We have

$$N^{-1} \left[\left(e_0 + \sum e_j |\tau_{j0}|^2 \right) + 1/2 \sum \tau_{j0} V_{0j} + \sum_{i<j} \tau_{i0}^* \tau_{j0} V_{ij} + \text{c.c.} \right].$$

For simplicity, rewrite $\tau_{j0} = \tau_j$ ($j=1,2,3$) and express them as

$$(q_j + ip_j) / \left(1 - \sum q_i^2 + p_i^2 \right)^{1/2},$$

(τ_j is in an S^4 sphere). Then we have the coset-represented Hamiltonian as

$$e_0 \left[1 - \sum_{i=1}^3 (q_i^2 + p_i^2) \right] + \sum_{i=1}^3 e_i (q_i^2 + p_i^2) + \sum_{i=1}^3 V_{0i} q_i \times \left[1 - \sum (q_i^2 + p_i^2) \right]^{1/2} + \sum_{i \neq j \neq 0} V_{ij} (q_i q_j + p_i p_j).$$

To conform to the Huckel model, only the nearest-neighbor interaction will be considered. The action on site i , n_i ($i=1,2,3$) is $(q_i^2 + p_i^2)$, on site 0, n_0 , it is $1 - \sum_{i=1}^3 (q_i^2 + p_i^2)$. Since there is but one electron in the system, the conditions $(q_i^2 + p_i^2) \leq 1$ and $\sum (q_i^2 + p_i^2) \leq 1$ have to be met. The phase angle $\theta_i = \tan^{-1}(-p_i/q_i)$ shows the relative phase between the actions on site 0 and i . This can be related to the signs of the eigencoefficients C_0 , C_i of the Huckel orbitals. If C_0 and C_i are of comparative magnitudes and if they are of the same or opposite sign, then $\theta_i = 0$ or π , respectively. If C_i is zero, then $\theta_i = \pi/2$. If C_i is positive (suppose C_0 is positive) and very small, then θ_i is less than but very close to $\pi/2$. Similarly, if C_i is negative and close to zero then θ_i is close to but slightly larger than $\pi/2$. $\sqrt{n_i}$ is equivalent to $|C_i|$. These interpretations have been well established in our previous work [12]. In our numerical calculation, the site energy is set as $-8.1 \times 10^4 \text{ cm}^{-1}$ and V_{ij} is $-1.4 \times 10^4 \text{ cm}^{-1}$.

$H(q,p)$ offers us a continuous energy range by q_i , p_i running through the whole space under the constraints. It is interesting to note that the lowest and highest eigenenergies of the Huckel orbitals correspond to the lowest- and highest-

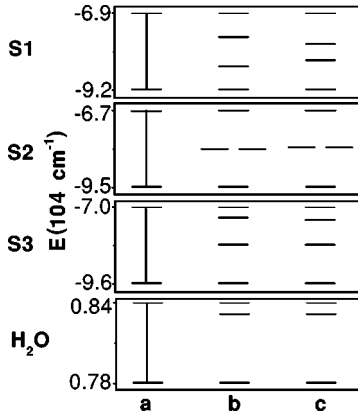


FIG. 2. Classical energy range by $H(q,p)$ (a) the quantized levels (b) and those by Lyapunov analysis (c) for $S1$, $S2$, and $S3$ structures and H_2O . $S1$, $S2$, and $S3$ (b) is by HMO. H_2O (b) is by the algebraic Hamiltonian.

energy values by $H(q,p)$. The elucidation of the quantized levels from $H(q,p)$ is our goal.

B. Quantization by minimizing the average Lyapunov exponent

Numerically, the classical energy range offered by $H(q,p)$ for various structures as shown in Fig. 2 are partitioned into 100 subdivisions. For the energy value at the center of each subdivision, there are numerous corresponding $(q_1, p_1, q_2, p_2, q_3, p_3)$ points. Two hundred randomly chosen $(q_1, p_1, q_2, p_2, q_3, p_3)$ points are employed to calculate the Lyapunov exponents. The exponents span a range and their average, denoted as $\langle \lambda \rangle$, is assigned formally to the corresponding energy level. For various structures, $\langle \lambda \rangle$ is plotted against the system energy as shown in Fig. 3. We propose that quantized energy levels are associated with the *local*

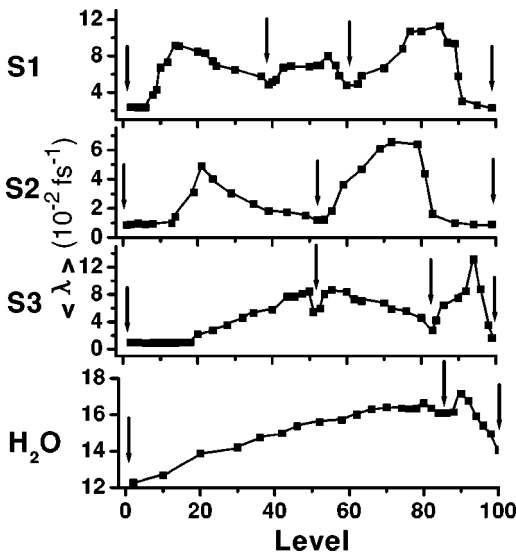


FIG. 3. Plot of the average Lyapunov exponent $\langle \lambda \rangle$ against the system energy for $S1$, $S2$, and $S3$ structures and H_2O . The arrows show the local minima of $\langle \lambda \rangle$. See text for details.

minima. Indeed, for each graph in Fig. 3, there are exactly four minima (except that for the $S2$ structure, there are three due to degeneracy). The quantized levels are shown in Fig. 2. They are quite consistent with those by the quantal HMO model. The quantization by minimizing the Lyapunov exponent shares the idea by Bohr and Gutzwiller that only a standing wave or periodic orbital can be stable and persistent in a quantal system. Classically, they correspond to the most stable trajectories and the least Lyapunov exponents. However, the algorithm adopted here does not rely on finding the periodic orbitals. Instead, those chaotic trajectories in the phase space that possess larger exponents contribute more to $\langle \lambda \rangle$. Hence, the proposed quantization condition calls for the least *global* chaoticity throughout the whole phase space. We also note that the precision of the identification of the quantized levels can be improved numerically by making finer partitions on the classical energy range by $H(q,p)$.

The quantized level energies by the Lyapunov analysis are then employed to calculate $(q_1, p_1, q_2, p_2, q_3, p_3)$ and then $(\theta_1, \theta_2, \theta_3)$ and (n_0, n_1, n_2, n_3) . They span a range and the maximal values are chosen for comparison with those by HMO. Listed in Table I are the eigencoeficients by HMO, their signs as interpreted from $(\theta_1, \theta_2, \theta_3)$ and $(\sqrt{n_0}, \sqrt{n_1}, \sqrt{n_2}, \sqrt{n_3})$. It is seen that the signs predicted are consistent with those by HMO. Indeed, small eigencoeficients do correspond to θ_i very closely to $\pi/2$ and is shown as zero in the column of the predicted signs of C_i in Table I. The relative magnitudes of $\sqrt{n_i}$'s are also consistent with those of C_i 's though not so exactly. We note that minor discrepancies are also evident: sign of C_2 and $\sqrt{n_2}$, $\sqrt{n_3}$ of the third level of $S3$.

IV. QUANTIZATION OF THE VIBRATIONAL SYSTEM OF H_2O

The algebraic Hamiltonian of H_2O can be written as the sum of two parts

$$H_0 = \omega_s(n_s + n_t + 1) + \omega_b(n_b + 1/2) + X_{ss}[(n_s + 1/2)^2 + (n_t + 1/2)^2] + X_{bb}(n_b + 1/2)^2 + X_{st}(n_s + 1/2)(n_t + 1/2) + X_{sb}(n_s + n_t + 1)(n_b + 1/2),$$

$$H' = K_{st}(a_s^+ a_t + \text{H.c.}) + K_{sb}(a_s^+ a_b a_b + a_t^+ a_b a_b + \text{H.c.}).$$

Here, subscripts s , t , and b stand for the two equivalent stretching and bending modes, respectively. n denotes the action. ω , X are the harmonic and anharmonic coefficients. H_0 is that part due to three nonlinear Morse oscillators. K_{st} and K_{sb} are the coupling strengths of the 1:1 resonance between the two stretches and Fermi resonance among the two stretches and the bends, respectively. These values are tabulated in Ref. [20]. These coefficients were elucidated from the fit of the eigenenergies of the algebraic Hamiltonian with the experimental spectra. $P = n_s + n_t + n_b/2$, called the polyad number is preserved, though not individual n_s , n_t , and n_b .

TABLE I. The eigencefficients, their signs as interpreted from the phases and the magnitudes (square root) of the actions by the coset space algorithm for $S1$, $S2$, and $S3$ structures and H_2O . Levels are designated as L . See text for details.

Structure	Level	Eigencefficients (HMO) C_0, C_1, C_2, C_3	By the coset space algorithm	
			predicted signs of C_0, C_1, C_2, C_3	$\sqrt{n_0}, \sqrt{n_1}, \sqrt{n_2}, \sqrt{n_3}$
$S1$	$L1$	+0.37,+0.60,+0.60,+0.37	+, +, +, +	0.37, 0.60, 0.59, 0.37
	$L2$	+0.60,+0.37,-0.37,-0.60	+, +, 0, -	0.51, 0.48, 0.48, 0.51
	$L3$	+0.60,-0.37,-0.37,+0.60	+, -, -, +	0.51, 0.48, 0.48, 0.51
	$L4$	+0.37,-0.60,+0.60,-0.37	+, -, +, -	0.37, 0.59, 0.59, 0.37
$S2$	$L1$	+0.50,+0.50,+0.50,+0.50	+, +, +, +	0.50, 0.50, 0.49, 0.50
	$L2/L3$	+0.71,0,-0.71,0 0,+0.71,0,-0.71	+,0,-,0	0.50, 0.49, 0.49, 0.49
	$L4$	+0.50,-0.50,+0.50,-0.50	+, -, +, -	0.49, 0.50, 0.49, 0.50
	$S3$	$L1$	+0.52,+0.52,+0.61,+0.28	+, +, +, +
$L2$		+0.37,+0.37,-0.25,-0.82	+, +, 0, -	0.49, 0.48, 0.47, 0.53
$L3$		+0.71,-0.71,0,0	+, -, -, ~0	0.51, 0.51, 0.52, 0.44
$L4$		+0.30,+0.30,-0.75,+0.51	+, +, -, +	0.32, 0.32, 0.73, 0.50
H_2O		$C_{n_s}, C_{n_t}, C_{n_b}$	$C_{n_s}, C_{n_t}, C_{n_b}$	$\sqrt{n_s}, \sqrt{n_t}, \sqrt{n_b}$
	$L1$	+0.04, +0.04, +0.99	+, +, +	0.08, 0.08, 0.99
	$L2$	+0.71,+0.71,-0.06	+, +, 0	0.72, 0.57, 0.35
	$L3$	+0.71,-0.71,0	+, -, 0	0.72, 0.64, 0.17

Very similar to the electronic system, this boson Hamiltonian can be cast into the four-dimensional coset space [7,8,11,20] with the replacements $n_t = (q_t^2 + p_t^2)/2$, $n_b = (q_b^2 + p_b^2)/2$, $n_s = P - n_t - n_b/2$ for H_0 and $K_{st}(2n_s)^{1/2}q_t + K_{sb}\{\sqrt{n_s}(q_b^2 - p_b^2) + [q_t(q_b^2 - p_b^2) + 2p_t q_b p_b]/\sqrt{2}\}$ for H' . (q_t, p_t, q_b, p_b) are the coordinates of the S^3 coset sphere. The constraints are

$$(q_t^2 + p_t^2) \leq 2P, \quad (q_b^2 + p_b^2) \leq 4P.$$

For a sample calculation, P is set as one. Shown in Fig. 2 are the classical energy range by $H(q, p)$ (a) and the quantized levels (b) by the algebraic Hamiltonian for H_2O . As before, the classical energy range is partitioned into 100 subdivisions. Thereby, the average Lyapunov exponents $\langle \lambda \rangle$ were calculated as shown in Fig. 3 in which three quantized levels can be identified if they are required to possess minimal $\langle \lambda \rangle$, *locally*. Shown in Fig. 2 are also these levels. The consistency with the quantal model is apparent.

The signs of the eigencefficients and their magnitudes are found to be quite consistent with those predicted by the coset space algorithm. They are shown in Table I.

V. CONCLUDING REMARKS

It is demonstrated that discrete levels can be elucidated for the system of one electron in multisites by the semiclassical quantization of the classical coset-represented Hamiltonian through Lyapunov analysis. Thereby, action and angle can also be determined. Action and angle are related to $|C_i|^2$ and the relative signs among C_i 's. The results show consistent signs and magnitudes (at least in proportionality) with

C_i 's, as offered by quantal HMO. For the vibrational system of H_2O , the Lyapunov analysis also leads to consistent results with those by the quantal method. These two simple systems, one fermionic and the other bosonic, are chosen for the trial of the proposed algorithm. Other cases of one electron in three and two sites have also been tried and all show nice consistency with the quantal HMO. For the vibrational system of H_2O as P increases, the number of levels increases drastically and the calculation becomes lengthy. For these cases, accurate determination of Lyapunov exponents could be crucial for the success of this algorithm.

The success in the level quantization by minimizing the average Lyapunov exponent deserves attention. In our algorithm, all the trajectories in the phase space with the same energy were adopted without discrimination and their Lyapunov exponents were averaged to obtain $\langle \lambda \rangle$. The more chaotic trajectories with larger exponents contribute more to $\langle \lambda \rangle$. What we require is the least global chaoticity throughout the whole phase space. The problems then are: What trajectories indeed play the most essential role in this Lyapunov quantization algorithm and what causes the least global chaoticity. Though our work is on the coset-represented Hamiltonian, it is highly speculated that this quantization idea for the chaotic system can be prevailing. Its application to the general nonintegrable systems are therefore highly recommended. These deserve our further exploration.

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