HARMONIC OSCILLATOR IN QUANTUM ROTATIONAL SPECTRA: MOLECULES AND NUCLEI

I. M. Pavlichenkov

Russian Research Center "Kurchatov Institute", Moscow, 123182, Russia

Abstract

The mapping of a rotational dynamics on a harmonic oscillator one is considered. The method is used for studying the stabilization of the rigid top rotation around the intermediate moment of inertia axis by orbiting particle.

1 Introduction

The quantum rotation is a specific type of excitation of microscopic system: hadrons, nuclei, molecules, and even atoms. The rotational excitations of molecules and nuclei have been studied in more detail. Electronic excitations are much higher than vibrational ones for most so-called "normal" molecules. Therefore they may be described adequately in the Born-Oppenheimer approximation. There is no analog of the Born-Oppenheimer approximation for atomic nuclei. Yet the occurrence of the rotational bands with strong (nearly 100 single particles) E2-transitions between neighboring states shows the existence of the collective rotation. All nucleons participate cooperatively into this collective motion with internal degrees of freedom being frozen completely or partly. The rotational excitations are grouped into rotational bands having states characterized in simplest case of a rigid axially-symmetric top by the energy ($\hbar = 1$)

$$E = I(I + 1)/2\Im, \tag{1}$$

and quantum number I of the total angular momentum. $\Im$ is a moment of inertia. A simplest non-axial system is a rigid asymmetric top with the Hamiltonian

$$H = A_1 I_1^2 + A_2 I_2^2 + A_3 I_3^2, \tag{2}$$

where I_α are the projections of the total angular momentum operator on the BFF (body-fixed frame) axes $\alpha = 1, 2, 3$. The rotational constants $A_\alpha = 1/(2\Im_\alpha)$ depend on the principal moments of inertia $\Im_\alpha$. The rotational band of an asymmetric top consists of rotational multiplets, i.e., of the levels with the same value of the quantum number I. Besides I, these levels are characterized by the irreducible representations of the group $D_2 = \{1, \Re_1, \Re_2, \Re_3\}$, which contains the identity operator and three 180° rotations around the BFF axes $\Re_\alpha(\pi) = exp(-i\pi I_\alpha)$. The irreducible representations of D_2 are labeled a_1, a_2, b_1, b_2. They correspond to the eigenvalues $r_\alpha = \pm 1$ of the operators $\Re_\alpha$. The subscripts 1 and 2 label even and odd symmetry levels with respect to the $\Re_2$ rotation, a and b label even and odd symmetry levels with respect to the $\Re_3$ rotation. Note that $r_1 r_2 r_3 = 1$ is true for each four representations.

Different methods are used to solve the Hamiltonian (2). As the first step we will calculate the classical rotation energy E as the function defined in the system phase space (a rotational energy surface). The phase space of a rotational motion is formed by three Euler angles ϕ, ϑ, ψ and three conjugated momenta $p_\phi, p_\vartheta, p_\psi$. The absolute value of the angular momentum I and its projection $I_z = p_\phi$ on the z-axis of the space-fixed frame are the integrals of motion. It is suitable to do the canonical transformation [1] to new conjugated variables I and q_I, I_z and q_z, I_3 and q. Since q_I and q_z are cyclic variables, the phase space of a rotational motion is two-dimensional. It is convenient to map it on the surface of the sphere of the I radius with a center in the origin of the BFF. The point on the sphere with coordinates θ and φ determines the orientation of the vector $\mathbf{I}$ in the BFF. The canonical transformation enables us to relate the conjugated variables I_3 and q to the angles θ and φ. For $I_z = q_I = 0$ and an arbitrary q, we have $\cos\theta = I_3/I$, $\varphi = \frac{\pi}{2} - q$. Thus, the trajectories of the tip of $\mathbf{I}$ on the phase sphere are classical trajectories of the system in its rotational phase space. When the rotational energy is close to $A_1 I^2$ or $A_3 I^2$, where A_1 and A_3 correspond to the smallest or the largest moment of inertia, the classical trajectories are small ellipses around axes 1 or 3. They represent precession motion around these axes. The trajectories close to axis 2 with the intermediate moment of inertia are unclosed. They represent unstable motion. A small deviation from this axis takes a top away from it.

2 Precession motion

Let us begin with classical precession. It is described by the Euler equations

$$\dot{I}_\alpha = \{H,\ I_\alpha\},\ \alpha = 1, 2, 3, \tag{3}$$

for the projections of the vector $\mathbf{I}$ on the BFF axes. In this equation $\{\ldots\}$ are the Poisson brackets. Let us introduce the classical concept of stationary rotation axis defined by the three equations $\{H,\ I_{0\alpha}\} = 0$. The stationary states $\mathbf{I}_0$ are identical with the fixed points of the energy surface. There are three stationary axes coinciding with the principal axes of a rigid top. For small precession around axis 1 ($I_1 \approx I$; $I_2, I_3 \ll I$) Eqs. (3) have the form

$$\begin{aligned}\dot{I}_2 &= -(A_3 - A_1)II_3, \\ \dot{I}_3 &= (A_2 - A_1)II_2.\end{aligned} \tag{4}$$

They describe a harmonic oscillation motion

$$I_2(t) = i_0\sqrt{A_3/A_1 - 1}\cos\omega_{11}t,\ \ I_3(t) = -i_0\sqrt{A_2/A_1 - 1}\sin\omega_{11}t, \tag{5}$$

with small amplitude i_0 and frequency

$$\omega_{11} = 2I\sqrt{(A_2 - A_1)(A_3 - A_1)}. \tag{6}$$

In the BFF, the $\mathbf{I}$ vector precess around axis 1 and, in the laboratory frame, the top precess around the angular momentum $\mathbf{I}$. It follows from the stability condition $\omega^2 > 0$ that the precession motion around the axis with the smallest or the largest moment of inertia is stable and around the axis with the intermediate one is unstable.

To obtain the energy level structure of a rotational band corresponding to a precession motion one must quantize this motion. It can be done by different methods.

Holstein-Primakoff Representation of Angular Momentum Operators. The method developed by Marshalek for a quantized rotator [2] is based on the one boson realization of angular momentum operators [3]

$$I_1 = I - b^+ b, \quad I_+ = I_2 + iI_3 = b^+ \sqrt{2I - b^+ b} = (I_-)^+,$$ (7)

in the space of wavefunctions

$$\varphi_{I\nu} = \sum_{K=-I}^{I} a_{K\nu} \frac{(b^+)^{I-K}}{[(I-K)!]^{1/2}} \mid 0\rangle,$$ (8)

where ν is the quantum number of a state in a rotational multiplet. The state $\mid 0\rangle$ corresponding to $K = I$ is a vacuum state of the boson creation and annihilation operators b^+, b. For describing precession motion we expand the square-root operator in I_+ and I_- in the series of a small quantity $\hat{n}/I$, where $\hat{n} = b^+ b$ is the boson number operator. In the harmonic approximation $(n \ll I)$, the Hamiltonian (2) is quadratic in boson operators

$$H = A_1 I^2 + \frac{I}{2}(A_2 + A_3) + I(A_2 + A_3 - 2A_1)b^+ b + \frac{I}{2}(A_2 + A_3)(b^+ b + bb).$$ (9)

The Hamiltonian (9) can be diagonalized by a canonical transformation

$$b = u\beta + v\beta^+, \quad \mid u \mid^2 - \mid v \mid^2 = 1,$$ (10)

to new boson operators β and β^+. The energy of the lowest levels is given by

$$E_{In} = A_1 I(I+1) + \omega_{11}(n + 1/2), \quad n = 0, 1, 2, \ldots .$$ (11)

The quantum number n describes the precession motion. For the state with $n = 0$ the wave function

$$\varphi_{I0} = \mid u \mid^{-1/2} \exp\left(\frac{v}{2u} b^+ b^+\right) \mid 0\rangle,$$ (12)

localizes near rotational axis 1. It corresponds to the sharply localized orientation of the angular momentum **I** along the positive direction of axis 1. Eq. (12) is not the eigenfunction of D_2 symmetries. Thus, the harmonic approximation is a "symmetry-breaking approximation." Being a linear theory it cannot describe tunneling the vector **I** through a potential barrier separating two degenerate minima.

Bargmann Representation [4]. Let us consider the complex variable

$$\zeta = x + iy = e^{i\varphi} \cot \frac{\theta}{2},$$ (13)

which is the stereographic projection of a point on the phase sphere with polar angles θ and φ on the plane passing through the south pole. As shown in Ref. [5], it is possible to construct the $SU(2)$ group representation in the space of the polynomials

$$\varphi(\zeta) = \sum_{K=-I}^{I} a_K \zeta^{I+K}.$$ (14)

The angular momentum operators in this representation have the form

$$I_1 = I\zeta + \frac{1}{2}(1 - \zeta^2)\frac{d}{d\zeta}, \quad I_2 = -iI\zeta + \frac{i}{2}(1 + \zeta^2)\frac{d}{d\zeta}, \quad I_3 = -I + \zeta\frac{d}{d\zeta}. \tag{15}$$

Many problems in nuclear and molecular physics can be treated by this approach [6]. With the operators (15), the Schrödinger equation for a top is reduced to the Heine equation [7]. To describe for example the precession motion around axis 3 we should consider the approximation $|\zeta| \ll 1$.

Approximate Solution of Reccurence Relations. This method is based on the approximation of recurrence relations by a second-order differential equation for high-I values [8]. The eigenfunction of the Hamiltonian (2) can be written in the form

$$\Psi_{IM\nu} = \sum_{K=-I}^{I} a_{IK\nu} D_{MK}^{I}(\vartheta), \tag{16}$$

where M and K are the quantum numbers of the operators I_z and I_3 respectively. D_{MK}^{I} is the Wigner function depending on the Euler angles ϑ. For the coefficients $a_{IK\nu}$, the three-term recurrence relation is obtained

$$P_K a_{I,K-2,\nu} + (H_{KK} - E_{I\nu})a_{IK\nu} + P_{K+2}a_{I,K+2,\nu} = 0, \tag{17}$$

where

$$
\begin{aligned}
H_K &= H_{KK} = \tfrac{1}{2}(A_1 + A_2) + \tfrac{1}{2}(2A_3 - A_1 - A_2)K^2, \\
P_K &= H_{KK-2} = \tfrac{1}{4}(A_1 - A_2)[(I - K + 2)(I + K - 1)(I - K + 1)(I + K)]^{1/2}.
\end{aligned}
\tag{18}
$$

By using the small parameter $\delta = [I(I + 1)]^{-1/2}$ let us introduce the continuous variable $k = K\delta$. We will treat the coefficients P and H as the smooth functions of this variable. As a result, the recurrence relation (17) may be rewritten in the form of the Schrödinger equation

$$I(I + 1)\mathbf{H}a_{I\nu}(k) = E_{I\nu}a_{I\nu}(k), \tag{19}$$

with the Hamiltonian

$$\mathbf{H} = [P(k + 2\delta) + P(k)]\cos 2\hat{p}\delta + i[P(k + 2\delta) - P(k)]\sin 2\hat{p}\delta + H(k), \tag{20}$$

where $\hat{p} = -id/dk$ is the canonically conjugated momentum to the coordinate k.

In the harmonic approximation $K \ll I$, Eq. (19) is reduced to the second-order differential equation

$$\frac{d^2 a_{I\nu}}{dK^2} + 2m[E - A_1 I(I + 1) - V(K)]a_{I\nu} = 0, \tag{21}$$

in the space of quantum numbers K. The equation describes the motion of the angular momentum **I** with effective mass $m = 1/[2(A_2 - A_1)I(I + 1)]$ in potential $V(K) = (A_3 - A_1)K^2$. This harmonic oscillator has the energy spectrum (11) and the wave function

$$a_{In} = \left[\frac{2}{2^n n!}\sqrt{\frac{2w}{\pi(2I + 1)}}\right]^{1/2} H_n\left(K\sqrt{\frac{2w}{2I + 1}}\right)\exp\left(-\frac{wK^2}{2I + 1}\right), \tag{22}$$

where $w = [(A_3 - A_1)/(A_2 - A_1)]^{1/2}$, and H_n is the Hermite polynomial. We have again a sharp localized state with broken symmetry.

The rotational dynamics of real many-body systems is more complicated than that of a rigid top because of the centrifugal and Coriolis forces. However the harmonic approximation can be used in this chase to understand the physical nature of the phenomenon under study. The example is bifurcations in quantum rotational spectra considered in Ref. [9]. In the next section we consider another problem having a bearing on a precessional motion.

3   Precession Motion around Intermediate Moment of Inertia Axis

As we proved above, the rotation of a rigid top around the intermediate axis is unstable. This is not a case if a system has additional degrees of freedom apart from rotational ones. We are going to consider a particle coupled with an asymmetric rigid top. This is the situation of one-electron Rydberg states in triatomic molecules, such as H_2O [10], and rotational bands in odd deformed nuclei [11].

The Born-Oppenheimer approximation breaks down in the molecular Rydberg spectra. As the total angular momentum I increases, the rotational levels pass from Hund's case (a) or (b) (the strong-coupling scheme), where the electronic splitting is large compared with the rotational one, to the Hund's case (d) (the weak-coupling scheme), where it is small. The model of an isolated j-complex is widely used for the description of the transition from strong to weak coupling in nuclear [11] and molecular [12] physics. This approximation is valid if coupling the states of a j-complex with other Rydberg states is small compared to the Coriolis coupling. The assumption means that one-particle angular momentum $\mathbf{j}$ is an integral of motion. As I increases, the momentum $\mathbf{j}$ decouples from the molecular ion core and couples to the axis of rotation with the maximal moment of inertia.

Let us consider the effective Hamiltonian describing the two degrees of freedom: rotational and one-particle. The rotational part of the Hamiltonian is the kinetic energy of a rigid top. We will use the self-consistent field approximation for describing one-particle motion. The non-spherical part of this field can be written in terms of the particle multipole momenta $q_{\lambda\mu}(\mathbf{r})$ as follows: $V = \sum_{\lambda\mu} Q_{\lambda\mu} q_{\lambda\mu}(\mathbf{r})$, where λ-values are even for the reflection symmetric field. For an isolated j-complex, the one-particle part of the Hamiltonian can be expressed in terms of the spherical tensor operators $T_{\lambda\mu}(\mathbf{j})$. Thus, the effective Hamiltonian of the system for an isolated j-complex is algebraic with symmetry $SU(2) \otimes SU(2)$. We consider this Hamiltonian in the quadrupole approximation when the components of mean field V with $\lambda > 2$ are smaller than the ones with $\lambda = 2$. It is convenient to write the Hamiltonian in the coordinate system fixed by the principal inertia axes:

$$H = \sum_\alpha [A_\alpha (I_\alpha - j_\alpha)^2 + g_\alpha j_\alpha^2],\tag{23}$$

where $g_1 = -g_2 = (g_0 \sin\gamma)/\sqrt{3}$, $g_3 = g_0 \cos\gamma$ ($-\infty < g_0 < +\infty$, $0° < \gamma < 60°$) are the parameters of the quadroupole part of the self-consistent field, which is diagonal in the considered frame. In

133

classical mechanics, the system dynamics is described by the equations of motion:

$$\dot{I}_\alpha = -2\epsilon_{\alpha\beta\gamma}A_\beta(I_\beta - j_\beta)I_\gamma$$
$$\dot{j}_\alpha = 2\epsilon_{\alpha\beta\gamma}[-A_\beta(I_\beta - j_\beta) + g_\beta l_\beta]j_\gamma,$$
(24)

where repeated indexes are summed.

The stationary state $\mathbf{I_0}$ and $\mathbf{j_0}$ of Eqs. (24) is determined by the eight algebraic equations since the two integrals of motion $\mathbf{I}^2$ and $\mathbf{j}^2$ exist. Therefore, the stationary state with an arbitrary orientation does not exist. There are two types of stationary states of Eqs. (24), corresponding to the lowest level of the rotational multiplets. The three aligned states S_α: $I_\alpha = I$, $j_\alpha = j$, $\alpha = 1, 2, 3$ with the energy

$$E_\alpha = A_\alpha(I - j)^2 + g_\alpha j^2,$$
(25)

have the parallel vectors $\mathbf{I_0}$ and $\mathbf{j_0}$ aligned along axis α. In the three plane stationary states $S_{\alpha\beta}$, these vectors are placed in the $(\alpha\beta)$-plane. As I increases the sequence of stationary states S_α and $S_{\alpha\beta}$ with the minimal energy for given I leads to the aligned state with the maximal moment of inertia. The transition from aligned state S_α to plane one $S_{\alpha\beta}$ is accompanied by the bifurcation of the C_{2v}-type [9] at the critical angular momentum

$$I_{\alpha\beta} = j\left\{1 + \frac{g_\alpha - g_\beta}{2A_\alpha} + \left[\left(\frac{g_\alpha - g_\beta}{2A_\alpha}\right)^2 - \frac{(g_\alpha - g_\beta)A_\beta}{A_\alpha(A_\alpha - A_\beta)}\right]^{\frac{1}{2}}\right\}.$$
(26)

The index α denotes the axis from which the angular momenta $\mathbf{I_0}$ and $\mathbf{j_0}$ decouple, while index β denotes the axis to which they approach. Both indexes $(\alpha\beta)$ denote the plane, in which these vectors move for $j < I_{\alpha\beta} < I < I_{\beta\alpha}$. Another pair of critical momenta determines the similar bifurcation points in the region $I < j$. The expression for these values is the same as Eq. (26) except the sign before a square root. We will consider below only the region $I > j$ in the case when $A_1 < A_2 < A_3$, $g_0 > 0$.

The precessional motion near the stable stationary state is described by linearized set of Eqs. (24). Four linear differential equations describe two normal modes corresponding to the small harmonic oscillations of vectors $\mathbf{I}$ and $\mathbf{j}$. The frequencies of these modes are obtained as the roots of a biquadratic equation. We begin our consideration with the precession near the S_1-state in the weak-coupling limit $A_\alpha I \gg g_\alpha j$. To simplify expressions let us use assumption $I \gg j$. The precessional mode with smaller frequency ω_{11} (6) represents the precession of the vectors $\mathbf{I}$ and $\mathbf{j}$ with different amplitudes. While the $\mathbf{I}$ vector circumscribes according to Eqs. (5) an elliptical cone around axis 1 with the amplitude i_0, the amplitude of the $\mathbf{j}$ vector is j/I times smaller that of the $\mathbf{I}$ one. Thus, this mode involves the precession of core angular momentum vector $\mathbf{R} = \mathbf{I} - \mathbf{j}$, which coincides, in considered approximation, to rigid top precession. Another normal mode with the frequency $\omega_{12} = 2IA_1$, which is equal to the core angular velocity around axis 1, involves the uniform rotation of the angular momentum vectors around this axis with identical amplitudes:

$$I_2(t) = j_2(t) = i_0 \cos \omega_{12}t, \quad I_3(t) = j_3(t) = i_0 \sin \omega_{12}t.$$
(27)

Consequently the momentum $\mathbf{R}$ does not participate in this motion.

Now we consider precession near the stationary state S_2, corresponding to the central axis. An orbiting particle stabilizes this state due to the anisotropic (quadrupole) interaction with a top.

The small values of $(A_2 - A_1)/A_2$ favors stability of the aligned state S_2 lowering its energy E_2 relative to E_1 (see Eq.(25)). To clarify the physical picture we will use the approximations $I >> j$ and $(A_2 - A_1)/A_1 << 1$ in describing precessional motion. The smaller frequency

$$\omega_{21} = 2\left[(A_2 - A_1)(A_3 - A_2)(I_{21}^2 - I^2)\right]^{1/2} \tag{28}$$

vanishes at the critical momentum I_{21} (26). The time-dependence of the angular momentum components for this mode is defined by

$$\begin{aligned} I_1(t) &= i_0\left[A_3/A_2 - 1\right]^{1/2}\cos\omega_{21}t, \\ I_3(t) &= -i_0\left[(A_2/A_1 - 1)(I_{21}^2/I^2 - 1)\right]^{1/2}\sin\omega_{21}t, \end{aligned} \tag{29}$$

and $\mathbf{j}(t) = (j/I)\mathbf{I}(t)$. The interpretation of this result is straightforward. Since the amplitude of the j-vector is small compared to that of the $\mathbf{I}$ ones, the considered mode represents the precession of the core angular momentum $\mathbf{R}$ similar to the rigid top precession (5). Yet unlike the latter, the tips of vectors $\mathbf{I}$ and $\mathbf{j}$ move on elliptic orbits stretched along axis 1 if the angular momentum I is close to I_{21}. This is just a consequence of the bifurcation, which shifts the angular momentum vectors into the (12)-plane. For another normal mode of frequency $\omega_{22} = 2IA_2$, the time-dependence of angular momentum components has the same form as in Eq. (27).

Thus, we have shown that the precession motion around the axis with intermediate moment of inertia is possible for a system consisting of a particle anisotropically coupled with an asymmetric top. The isolated j-complex approximation is used in considering this phenomenon. To examine it one can solve the classical equation of motion for a particle coupled with an asymmetric top without this restriction. The equations involve two different time scales: fast particle motion and slow core rotational motion. After averaging on the fast motion, one can obtain the closed set of nine equations for components of $\mathbf{I}$ and particle angular and quadrupole momenta. The averaged equations can describe the stabilization phenomenon and the precession around intermediate axis. This insight into the problem reveals the close relationship of our stabilization effect with that of the Kapitza pendulum [13]. Another intriguing analogy is the new discovery in planetary science where it has been shown recently [14] that the Moon stabilizes the chaotic wobble of the Earth's rotational axis, which is unstable due to orbital coupling with other planets. Thus, without the Moon, large variations in obliquity resulting from the chaotic wobble might have driven dramatic changes in the Earth's climate. There are two fundamental distinctions of our problem from considered above: we deal with the *isolated and quantum* system.

The above found precessional frequencies are associated with the splitting between the lowest levels of a multiplet. To obtain this result one must quantize the precession motion. It can be done by using the Holstein-Primakoff representation. The result for lowest multiplet levels corresponding to the stationary state S_α is

$$E_{In} = E_\alpha(I) + \omega_{\alpha 1}(n_1 + 1/2) + \omega_{\alpha 2}(n_2 + 1/2) \tag{30}$$

where E_α is given by Eq. (25), and n_1 and n_2 are the numbers of bosons in corresponding mode. The boson operators b_k^+ and b_k connect the odd and even with respect to the C_2^α-transformation states inside a rotational multiplet. Consider, for example, the precession around axis 1 in the weak-coupling limit. In this approximation, any rotational multiplet (I-multiplet) consists of R-multiplets with the quantum numbers $R = I - j + m$, $m = 0, 1, ..., 2j$. The levels in R-multiplets

135

with the same quantum number R but different I are degenerated. The frequency (6) describing the precession of the **R**-vector is equal to the splitting between the lowest levels a_1 and b_1 (or a_2 and b_2) in a R-multiplet. Another frequency $\omega_{12} = 2IA_1$ is equal to the splitting between the lowest levels of adjacent R-multiplets belonging to the same I-multiplet. The situation for the precession around the intermediate axis is more complicated. According to the precessional approximation, the lowest states of a multiplet involve two groups of roughly equidistant levels, which are described by Eq. (30). But a smaller frequency vanishes in a critical point and the precessional approximation becomes inappropriate in this region. This means the redistribution of multiplet levels, which provides a method for the identification of the intermediate axis precession in an experiment.

Acknowledgments

References

[1] S. D. Augustin, and W. H. Miller, J. Chem. Phys. **61**, 3155 (1974).

[2] E. R. Marshalek, Phys. Rev. C **11**, 1426 (1975).

[3] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[4] V. Bargmann, Rev. Mod. Phys. **34**, 896 (1962).

[5] N. Ya. Vilenkin, *Special Functions and the Theory of Group Representations* (Am. Math. Soc. Translation, Providence, Rhode Island, 1968).

[6] I. M. Pavlichenkov, in: *Classical and Quantum Systems. Foundations and Symmetries. Proceedings of the II International Wigner Symposium, Goslar, 1991.* (World Scientific, Singapure, 1992), p. 357.

[7] I. M. Pavlichenkov, Sov. J. Nucl. Phys. **33**, 52 (1981).

[8] P. A. Braun, A. M. Shirokov, and Yu. F. Smirnov, Molec. Phys. 56, 573 (1985).

[9] I. M. Pavlichenkov, Physics Reports **226**, 175 (1993).

[10] R. H. Page, R. J. Larkin, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **88**, 2249 (1988).

[11] G. B. Hagemann and I. Hamamoto, Phys. Rev. C **40**, 2862 (1989).

[12] G. Herzberg, J. T. Hougen, and J. K. G. Watson, Can. J. Phys. **60**, 1261 (1982); R. D. Gilbert, M. S. Child, and J. W. C. Johns, Molec. Phys. **74**, 473 (1991).

[13] L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, Oxford, 1962).

[14] J. Laskar, F. Joutel, and P. Robutel, Nature **361**, 615 (1993).