

STABLE AND UNSTABLE ROVIBRATIONAL STATES OF A MOLECULE

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Stability of motions for different potential functions describing vibrational motions of rotating molecule has been discussed. It was shown that an equilibrium position for nonrotating r_0 and rotating r_J molecules for almost all the examined potentials is a node, but for the molecule described by the soft body model a critical value of rotation quantum number J_c occurs above which r_0 is a saddle point, and the stable motion may occur only around r_J .

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Stability or instability of motions plays an important role in many problems of physics, astronomy, molecular physics and is determined by the form of potential used to describe the problem considered [1-9].

In this paper I would like to discuss this problem for rotational-vibrational (rovibrational) motions which are described by many different potential functions (see for example [10, 11]). For this purpose eigenvalue λ of stability matrix A will be calculated for two fixed points r_0 and r_J [1, 5, 7]. When λ is a real and positive number, the fixed point is a repeller, whereas for an imaginary one, the motion examined is stable around this point which is a centre.

The elements of the stability matrix A_{ij} are calculated by the following method [1, 2, 5, 7]. Let us consider a motion described by the Hamiltonian

$$H = \sum_{i=1}^n \frac{p_i^2}{2m_i} + V(q_1, \dots, q_n),$$

where p_i is the generalized momentum for the i -th degree of freedom ($i = 1, \dots, f$), q_i is the generalized coordinate for the i -th independent motion ($i = 1, \dots, f$). Now

$$A_{kl} = \left(\frac{\partial F_k}{\partial x_l} \right)_{q_i^0}, \quad k = 1, \dots, f, \quad l = 1, \dots, f$$

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and for $k = 1, \dots, f$

$$F_k = \frac{\partial H}{\partial p_n}, \quad n = 1, \dots, f, \quad F_{f+n} = -\frac{\partial H}{\partial q_n},$$

$x_1, \dots, x_f = q_1, \dots, q_f, x_{f+1}, \dots, x_{2f} = p_1, \dots, p_f$; q_i^0 is the i -th fixed point.

The eigenvalues of the stability matrix are calculated from the equation

$$\text{Det}|A_{kl} - \lambda \delta_{kl}| = 0.$$

Let us consider an example as simple as possible, i.e. a one-dimensional harmonic oscillator with centrifugal force, now the Hamiltonian has the form

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kr^2 + \frac{R^2}{2\mu r^2}$$

and $F_1 = p/\mu$, $F_2 = -kr + R^2/(\mu r^3)$, the fixed point is obtained from the condition $F_2 = 0$, and is equal to $r_0^4 = R^2/\mu k$, now

$$A_{11} = \frac{\partial F_1}{\partial r} = 0, \quad A_{12} = \frac{\partial F_1}{\partial p} = \frac{1}{\mu},$$

$$A_{21} = \left(\frac{\partial F_2}{\partial r} \right)_{r_0} = -k - \frac{3R^2}{\mu r_0^4} = -4k, \quad A_{22} = 0.$$

The eigenvalue of problem for the case has the form

$$\begin{vmatrix} -\lambda & 1/\mu \\ -4k & -\lambda \end{vmatrix} = 0, \quad \text{so } \lambda^2 + \frac{4k}{\mu} = 0 \quad \text{and } \lambda = i\sqrt{\frac{4k}{\mu}},$$

has an imaginary value for r_0 so the fixed point is a node [1, 7].

Table I shows the results obtained for different potentials, as well as the role of rotation of the body considered in the destabilization or stabilization of motion. These results have been calculated for diatomic molecules, because for these species the potential which properly describes the internal motion is well known [10-12]. For these calculations the fixed point r_0 was obtained from the condition $\partial V/\partial r = 0$, whereas the second fixed point r_J was obtained from the overall equilibrium condition, i.e. from the following equation:

$$-\frac{\partial V}{\partial r} + \frac{R^3}{\mu r^3} = 0,$$

where $R^2/\mu r^3$ describes a force brought about by rotation of a molecule.

As follows from Table I the rotational motion of a molecule stabilizes the nodal feature of the fixed points r_0 and r_J . Interesting results have been obtained for a double minimum potential (see no. 5 in Table I) for which rotation of a molecule stabilizes r_0 (the point for which the potential has a maximum).

In a series of papers [13-19] it has been shown that the detected rovibrational transitions are very well assigned within the soft or deformable model, i.e. within the model which takes into consideration a deformation of a molecule brought about by its rotation. This model introduces the references configuration, i.e. the rigid configuration around which the nuclei perform their motions, from the condition

$$f_i = -\frac{\partial V}{\partial r} + m_i \omega \times \omega \times r_i, \quad (1)$$

TABLE I

Values of the stability matrix for different potentials.

	Potential	Fixed point	λ and remarks
1.	$\frac{1}{2kr^2} + \frac{R^2}{2\mu r^2}$	$r_J = \sqrt[3]{\frac{R^2}{\mu k}}$	i^a , r_J is a node
2.	$ar^2 + br^4, a, b > 0$	r_0 (min. of funct.)	i , r_0 is a node
3.	$ar^2 + br^4, a > 0, b < 0,$ and $2a + 12br_0^2 > 0$	r_0 (min. of funct.)	i , r_0 is a node
4.	$ar^2 + br^4, a > 0, b > 0$ and $2a + 12br_0^2 < 0$	r_0 (min. of funct.) $r_{1/2}$ (max. of funct.)	re^b , r_0 is a repeller i , $r_{1/2}$ are nodes
5.	$ar^2 + br^4 + \frac{R^2}{2\mu r^2}$	r_0	i , for $a > 0, b < 0$, and $2a - 12br_0^2 + \frac{3R^2}{\mu r_0^4} \geq 0$ re, for $2a - 12br_0^2 + \frac{R^2}{\mu r_0^4} < 0$
6.	$ar^2 + br^4 + \frac{R^2}{2\mu r^2}, R^2 > z$ $R^2 < z, z = \frac{4\mu a^3}{2ab^2}$	r_J r_{J1} r_{J2}, r_{J3}	i , r_J is a node, re, r_{J1} is a repeller, i , r_{J2}, r_{J3} are nodes
7.	$D(1 - e^{-\alpha x})^2, x = r - r_0$	r_0	i , r_0 is a node
8.	$D(1 - e^{-\alpha x})^2 + \frac{R^2}{2\mu x^2}$	r_0	i , r_0 is a node for $R^2 > z_1$ $z_1 = \frac{4}{3} D \alpha^2 \mu r_0^4 e^{-\alpha r_0} \left(\frac{1}{2} - e^{-\alpha r_0} \right)$ re, r_0 is a repeller for $R^2 < z_1$
9.	$D(1 - \frac{r}{r_0})^2 + \frac{R^2}{2\mu r^2}$	r_0 and r_J	i , r_0 and r_J are nodes

^a i — imaginary value of λ , ^bre — real value of λ .

where $f_i^0 = -\partial V/\partial r$ is a force acting upon the i -th atom of a molecule brought about by electronic structure of a molecule, and ω is the angular velocity of rotation of a molecular coordinate system relative to the laboratory one.

The solution of this equation, r_{iJ} , gives the equilibria positions which depend on the angular velocity ω . As a result the overall angular momentum is given by the equation

$$P_\alpha = \frac{\partial L}{\partial \omega_\alpha} = \sum [m_i(r_i \times \omega \times r_i)_\alpha + m_i(r_i \times v_i)_\alpha + (\partial r_{Ji}/\partial \omega_\alpha) \nabla_i L],$$

so $P_\alpha = R_\alpha + K_\alpha$, $\alpha = x, y, z$, where

$$K_\alpha = \sum_i \frac{\partial r_{Ji}}{\partial \omega_\alpha} \nabla_i L \quad (2)$$

is an additional angular momentum brought about by the changing of the distance of the i -th element of the soft body from the equilibrium position r_{iJ} due to vibrations (for $r = r_{iJ}$, $\nabla_i L = 0$ and $K_\alpha = 0$, see Eq. (1))[13].

For diatomic molecules

$$R = \mu r^2 \omega = P - K$$

and the Hamiltonian for internal motions has the following form [13, 14]:

$$H = \frac{p^2}{2\mu} + \frac{P^2 - K^2}{2\mu r^2} + V(r). \quad (3)$$

From this equation we see that internal motions of the soft body are described by the effective potential

$$V_{\text{ef}} = V(r) + \frac{P^2 - K^2}{2\mu r^2}. \quad (4)$$

The additional angular momentum is calculated from Eq. (2), i.e. from the equation

$$K = s \left[-\frac{\partial V}{\partial r} + \frac{(P - K)^2}{\mu r^3} \right],$$

where $s^2 = (\partial r_j / \partial \omega_x)^2 + (\partial r_j / \partial \omega_y)^2$. The solution of this equation leads to the following formula for additional angular momentum K :

$$K = \frac{\mu r^3 + A - d}{\kappa},$$

where $A = 4B_0 J(J+1)\mu r_0 r_J^2 / D$, $B_0 = h^2 / (2\mu r_0^2)$, $\kappa = \sqrt{8B_0 J(J+1)\mu r_J^4 / D^2}$, $d = \sqrt{\mu^2 r^6 + 2A\mu r^3 + 4A\mu r_J^2(r - r_0)}$ and r_J is obtained from Eq. (1) where the Fues-Kratzer [20, 21] potential has been applied for description of the internal motion. As a result $r_J = r_0[1 + B_0 J(J+1)/D]$, and D is a constant related to the dissociation energy of a molecule.

TABLE II

Eigenvalue of the stability matrix for Ar_2 ($1\Sigma_g^+$) calculated for two fixed points r_0 and r_J .

J	λ		remarks
	r_0	r_{J1}	
1	imaginary	imaginary	r_0 and r_J are nodes
112	imaginary	imaginary	r_0 and r_J are nodes
113	real	imaginary	r_0 is a saddle point, r_J is a node
120	real	imaginary	r_0 is a saddle point, r_J is a node

TABLE III

Dependence of the critical rotational quantum number J_c on $Y = B_0/D$.

Y	r_0	r_J	J_c
1.349×10^{-2}	saddle point	node	4
1.336×10^{-3}	saddle point	node	11
1.9046×10^{-5}	saddle point	node	113

Table II presents the results obtained for Ar_2 ($1\Sigma_g^+(0_g^+)$) molecule (the r_0 and D parameters used in these calculations have been taken from Ref. [13]). Table III shows the dependence of eigenvalue of the stability matrix λ on Y parameter

defined by the relation $Y = B_0/D$, and gives critical values of rotational quantum number J_c at which r_0 changes its character from a node to a saddle point.

From the above presented calculations the following conclusions may be drawn:

(1) for all the widely applied potentials, namely for the harmonic and non-harmonic ones, the two fixed points, r_0 and r_J , are nodes, and the motions around these points are stable,

(2) rotational motions preserve the character of r_0 for higher energies, i.e. rotation stabilizes the structure of a molecule (this is the well-known gyroscopic effect (see for example [5])),

(3) for the soft body model the character of the fixed points depends on rotational quantum number J . Below some J called the critical rotation quantum number J_c both fixed points, namely r_0 and r_J , are nodes, whereas above J_c the motion around r_0 is unstable (r_0 is a saddle point) but r_J is still a node, so a motion around this point is stable. As a consequence a molecule changes its shape above the critical value of J .

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