

# Classical approach to effective rotational energy and bifurcation in rotational dynamics of $H_2X$ molecules

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A classical method of effective rotational energy describing the molecular rotation is analyzed from the viewpoint of relative equilibria approach. Explicit formulas for the effective rotational energy up to sixth order in angular-momentum components are derived and compared with the results of quantum approach. The method is applied to get the analytical description of bifurcation in rotational dynamics of  $H_2X$  molecules without the suggestion of constant bond length.

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## I. INTRODUCTION

The classical description of molecular rotation has proved to be an important tool for understanding the qualitative features of rotational spectra in molecules [1]. The central role in this description is played by the notions of effective rotational energy [2] and rotational energy surface (RES), introduced by Harter and Patterson [3]. The effective rotational energy is a function of angular-momentum vector  $\mathbf{J}$  in a molecule-fixed frame which can be viewed as a generalization of the rigid body rotational energy incorporating the effects of centrifugal distortion. In the model of Harter and Patterson, effective rotational energy defines the dynamics of angular-momentum vector  $\mathbf{J}$  in a molecule-fixed frame through the equation, analogous to Euler equation for the rigid body rotation [3]. The qualitative features of this dynamics allow one to explain the structure of rotational multiplets in molecular spectra [1,3]

The effective rotational energy can be viewed as a classical analog of the quantum effective rotational Hamiltonians describing the rotation energy levels for a separate vibronic state in a molecule [4,5]. One can obtain the effective rotational energy substituting the operators of angular-momentum components by the corresponding classical variables [1]. We will refer to this approach to effective rotational energy as a quantum approach.

Another method of obtaining the effective rotational energy is based on purely classical consideration; it traces back to the work of Wilson [6]. The centrifugal distortion in a molecule can be described by means of effective potential which contains the centrifugal term depending on angular-momentum vector  $\mathbf{J}$ . In this approach the value of effective rotational energy for some vector  $\mathbf{J}$  is defined by the minimum of corresponding effective potential. The applications of this method to different systems were considered by Petrov *et al.* [7–9]. A similar approach was used also in Ref. [10].

In this paper we analyze the classical approach to effective rotational energy and discuss its relationship with the

quantum approach. Our main tool is the notion of relative equilibrium in a molecule [11–14]. Under the relative equilibrium the system of nuclei rotates around the motionless axis with constant internuclear distances and angular velocity. We find that in the Wilson's approach the stationary points on RES correspond exactly to relative equilibria. Considering the relationship between the classical and quantum approaches to effective rotational energy, we find that these give the same result for the terms up to the sixth order in effective rotational energy. In most cases the qualitative picture of relative equilibria at small  $J$  is completely determined by these terms [1,10,12].

In some cases the classical approach can give an additional insight into the problem. An example of this provides the effect of bifurcation in rotational dynamics of  $H_2X$  molecules [15]. This effect was predicted in the work of Zhilinskii and Pavlichenkov [16] on the basis of a classical analysis of a rigid bender model in which  $X-H$  bonds are "frozen." Later the numerical calculations provided more detailed description of this bifurcation [8,17,18].

In this paper we apply the method of effective rotational energy in order to obtain the analytical description of bifurcation in  $H_2X$  molecules without imposing the constraints on the bonds. The analysis of the rigid bender model brings forth the conclusion that the leading role in the problem is played by a configuration in which a molecule becomes an accidental symmetric top [1]. In particular, if we consider this special configuration as an equilibrium configuration of a hypothetical molecule then the bifurcation occurs at  $J=0$ . This hypothetical molecule is a very appropriate example for a more detailed analysis, which we consider here. Using some natural assumptions we find the simple sufficient condition of bifurcation appearance: the frequency of bending mode should be less than the frequencies of stretching modes. On the basis of these results we give the description of the bifurcation in real  $H_2X$  molecules.

This paper is organized as follows. In Sec. II we analyze the classical construction of effective rotational energy. The general scheme of its expansion in angular momentum components is developed in Sec. III in which the comparison with the results of the quantum approach is done also. Section IV is devoted to the problem of bifurcation in  $H_2X$  molecules.

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## II. EFFECTIVE ROTATIONAL ENERGY

### A. Relative equilibria in molecules

The intramolecular dynamics can be described by the following system of equations [13,14]

$$\begin{aligned}\dot{q}_k &= \frac{\partial H}{\partial p_k}, \\ \dot{p}_k &= -\frac{\partial H}{\partial q_k}, \\ \dot{\mathbf{J}} &= \mathbf{J} \times \frac{\partial H}{\partial \mathbf{J}},\end{aligned}\quad (1)$$

where  $(q_1, \dots, q_{3N-6}) = q$  are the internal coordinates,  $(p_1, \dots, p_{3N-6}) = p$  the conjugated momenta,  $\mathbf{J}$  the angular-momentum vector in the molecule-fixed frame, and  $H(\mathbf{J}, q, p)$  the Hamilton function. The angular momentum  $\mathbf{J}$  and momenta  $p_k$  can be expressed through the angular velocity in the molecule-fixed frame  $\boldsymbol{\omega}$  and  $\dot{q}_k$ :

$$\mathbf{J} = \mathbb{I} \left( \boldsymbol{\omega} + \sum_k \mathbf{A}_k \dot{q}_k \right), \quad (2)$$

$$p_k = \sum_l g_{kl} \dot{q}_l + (\mathbf{A}_k, \mathbf{J}), \quad (3)$$

where  $\mathbb{I}_{\alpha\beta}(q)$  is the inertia tensor in the molecule-fixed frame,  $\mathbf{A}_k(q)$  the gauge potential, and  $g_{kl}(q)$  the metric tensor of the shape space [19]. The stationary points of system (1) correspond to relative equilibria [11–14]. As follows from Eqs. (2) and (3), relative equilibria are solutions, under which the system of nuclei rotates around the motionless axis with constant internuclear distances and angular velocity. (We consider the relative equilibria with only noncollinear configurations.)

Using the explicit form of Hamilton function  $H(\mathbf{J}, q, p)$ , the conditions on relative equilibria can be obtained. This can most easily be done using the Hamilton function in the form developed by Herschbach and Laurie [20] (see also Ref. [19]). The resulting conditions are as follows [14]:

$$(p_k)_e = (\mathbf{A}_k(q_e), \mathbf{J}_e), \quad (4)$$

$$\mathbb{I}^{-1}(q_e) \mathbf{J}_e = \lambda \mathbf{J}_e, \quad (5)$$

$$\frac{\partial U}{\partial q_k}(\mathbf{J}_e, q_e) = 0, \quad U(\mathbf{J}, q) = \frac{1}{2}(\mathbf{J}, \mathbb{I}^{-1}(q) \mathbf{J}) + V(q), \quad (6)$$

where  $V(q)$  is the adiabatic potential and  $U(\mathbf{J}, q)$  the effective potential. From condition (4) we see that the equilibrium values of momenta  $p_e$  are completely determined by the values  $q_e$  and  $\mathbf{J}_e$ . Equation (5) implies that the vector  $\mathbf{J}_e$  should be directed along the principal axis of inertia of relative equilibrium configuration. Condition (6) tells us that relative equilibria configurations should correspond to the stationary points of effective potential containing the centrifugal term.

In order to find the relative equilibria it is necessary to solve the system of Eqs. (5) and (6) [13].

Condition (6) traces back to the work of Wilson [6]. However, Wilson uses the conditions  $p_k = 0$  instead of  $\dot{q}_k = 0$  and this results in the appearance of effective inverse inertia tensor  $\mu(q)$  instead of  $\mathbb{I}^{-1}(q)$  in Eq. (6). Fortunately, this has no effect on the terms of fourth order in effective rotational energy considered in Ref. [6].

### B. Effective rotational energy

Now we turn to the classical construction of effective rotational energy [6–8,10]. Let  $(q_1^0, \dots, q_{3N-6}^0) = q_0$  be a nondegenerate minimum point of adiabatic potential  $V(q)$ . For sufficiently small  $J = |\mathbf{J}|$  an effective potential  $U(\mathbf{J}, q)$  as a function of  $q$  has a unique minimum point in the vicinity of  $q_0$ . Let  $(Q_1(\mathbf{J}), \dots, Q_{3N-6}(\mathbf{J})) = Q(\mathbf{J})$  be the coordinates of this point and  $h(\mathbf{J}) = U(\mathbf{J}, Q(\mathbf{J}))$  the corresponding minimal value of effective potential which is by the definition a value of effective rotational energy for this  $\mathbf{J}$  [6,8]. For all the pairs  $(\mathbf{J}, Q(\mathbf{J}))$  condition (6) is fulfilled, but to relative equilibria correspond only those pairs for which also condition (5) holds:

$$\mathbb{I}^{-1}(Q(\mathbf{J}_e)) \mathbf{J}_e = \lambda \mathbf{J}_e. \quad (7)$$

On the other hand, from the definition of  $h(\mathbf{J})$  we have

$$\frac{\partial h}{\partial \mathbf{J}} = \frac{\partial U}{\partial \mathbf{J}}(\mathbf{J}, Q(\mathbf{J})) + \sum_k \frac{\partial U}{\partial q_k}(\mathbf{J}, Q(\mathbf{J})) \frac{\partial Q_k}{\partial \mathbf{J}} = \mathbb{I}^{-1}(Q(\mathbf{J})) \mathbf{J}. \quad (8)$$

Consequently, Eq. (7) can be written in the form

$$\frac{\partial h}{\partial \mathbf{J}}(\mathbf{J}_e) = \lambda \mathbf{J}_e. \quad (9)$$

Let  $h_J$  be the restriction of  $h(\mathbf{J})$  to the sphere  $|\mathbf{J}| = J$  [as a function of two angles  $(\theta, \phi)$ ]. We can interpret condition (9) as a stationary condition for the function  $h_J$  with  $\lambda$  being the Lagrange multiplier.

We arrive at the following conclusion: for sufficiently small  $J$  the relative equilibria with configurations near  $q_0$  are defined by stationary points of function  $h_J$ . Such stationary points define the orientations of vector  $\mathbf{J}_e$  (with fixed  $J$ ) and corresponding configurations of relative equilibria are given by the equation  $q_e = Q(\mathbf{J}_e)$ . Thus we see that the method of effective rotational energy has a natural interpretation in terms of relative equilibria.

It is interesting to compare this result with the model of Harter and Patterson [3]. In this model, effective rotational energy  $h(\mathbf{J})$  defines the dynamics of vector  $\mathbf{J}$  by means of equation analogous to Euler equation for the rigid body rotation:

$$\dot{\mathbf{J}} = \mathbf{J} \times \frac{\partial h}{\partial \mathbf{J}}. \quad (10)$$

Since the length of vector  $\mathbf{J}$  is conserved, its dynamics is completely determined by the corresponding restriction

$h_J(\theta, \phi)$ , the radial plot of which in three-dimensional space is called rotational energy surface (RES). The stationary points of  $h_J(\theta, \phi)$  correspond to stationary solutions for vector  $\mathbf{J}$ . Though this model is only approximate [since in fact the dynamics of vector  $\mathbf{J}$  is coupled with vibrational dynamics by means of a system (1)], we see that the stationary solutions of Eq. (10) have an *exact* meaning of relative equilibria.

In the work of Montaldi and Roberts [12] a rather general theory is applied to the analysis of relative equilibria in molecules. In particular, they prove that there exists a function with the properties of  $h(\mathbf{J})$ . The Wilson's approach is perhaps less general, but it provides more explicit and simple construction.

### III. EXPANSION OF EFFECTIVE ROTATIONAL ENERGY

In order to get explicit formulas for effective rotational energy we consider its expansion in a series in angular momentum components  $J_\alpha$ . In this section we describe the general scheme of this expansion and derive explicit formulas for the terms up to sixth order. Then we compare our results with analogous formulas for the terms in effective rotational Hamiltonians.

#### A. The general scheme of expansion

The series expansions for the functions  $h(\mathbf{J})$  and  $Q_k(\mathbf{J})$  have the form

$$h(\mathbf{J}) = h(0) + h^{(2)}(\mathbf{J}) + h^{(4)}(\mathbf{J}) + \dots, \quad (11)$$

$$Q_k(\mathbf{J}) = q_k^0 + Q_k^{(2)}(\mathbf{J}) + Q_k^{(4)}(\mathbf{J}) + \dots, \quad (12)$$

where the numbers in parentheses indicate the order in angular-momentum components. The invariance of  $h(\mathbf{J})$  and  $Q_k(\mathbf{J})$  under inversion  $\mathbf{J} \rightarrow -\mathbf{J}$  (following immediately from their definition) implies the absence of odd order terms in these expansions.

To derive explicit formulas for the terms in expansions (11) and (12) it is convenient to use the following trick: to proceed as if there is only one internal coordinate  $q$ . It will be obvious from the procedure of derivation that the general formulas can be obtained from the simplified ones by adding indices for internal coordinates and sums over them.

We start with the Taylor expansions for effective potential and its first derivative in the vicinity of  $q_0$ :

$$\begin{aligned} U(\mathbf{J}, q) &= C(\mathbf{J}, q) + V(q) \\ &= C(\mathbf{J}, q_0) + V(q_0) + C_1 \delta q + \frac{1}{2}(C_2 + V_2) \delta q \delta q + \dots, \end{aligned} \quad (13)$$

$$\frac{\partial U}{\partial q} = C_1 + (C_2 + V_2) \delta q + \frac{1}{2}(C_3 + V_3) \delta q \delta q + \dots, \quad (14)$$

where  $C = \frac{1}{2}(\mathbf{J}, \Gamma^{-1}(q)\mathbf{J})$  is a centrifugal term in effective potential,  $C_n$  and  $V_n$  are derivatives of centrifugal term and

adiabatic potential respectively, and  $\delta q = q - q_0$ . Substituting expansion (12) into Eq. (14) and collecting the terms of the same order in components of  $\mathbf{J}$ , we obtain

$$\begin{aligned} \left. \frac{\partial U}{\partial q} \right|_{q=Q(\mathbf{J})} &= C_1 + V_2 Q^{(2)} + C_2 Q^{(2)} + V_2 Q^{(4)} + \frac{1}{2} V_3 Q^{(2)} Q^{(2)} \\ &\quad + C_2 Q^{(4)} + V_2 Q^{(6)} + \frac{1}{2} C_3 Q^{(2)} Q^{(2)} \\ &\quad + V_3 Q^{(2)} Q^{(4)} + \frac{1}{3!} V_4 Q^{(2)} Q^{(2)} Q^{(2)} + \dots. \end{aligned} \quad (15)$$

By the definition of  $Q(\mathbf{J})$  the result of this substitution should be zero; therefore, the terms of each order in expansion (15) vanish. Using this we find

$$\begin{aligned} Q^{(2)} &= -V_2^{-1} C_1, \\ Q^{(4)} &= -V_2^{-1} \left( C_2 Q^{(2)} + \frac{1}{2} V_3 Q^{(2)} Q^{(2)} \right), \\ Q^{(6)} &= -V_2^{-1} \left( C_2 Q^{(4)} + \frac{1}{2} C_3 Q^{(2)} Q^{(2)} + V_3 Q^{(2)} Q^{(4)} \right. \\ &\quad \left. + \frac{1}{3!} V_4 Q^{(2)} Q^{(2)} Q^{(2)} \right). \end{aligned} \quad (16)$$

The formulas for the terms in expansion (11) are obtained by substitution of expansion (12) into Eq. (13):

$$\begin{aligned} h^{(2)} &= C(\mathbf{J}, q_0), \\ h^{(4)} &= C_1 Q^{(2)} + \frac{1}{2} V_2 Q^{(2)} Q^{(2)} = -\frac{1}{2} V_2^{-1} C_1 C_1, \\ h^{(6)} &= \frac{1}{2} C_2 Q^{(2)} Q^{(2)} + \frac{1}{3!} V_3 Q^{(2)} Q^{(2)} Q^{(2)}, \quad (17) \\ h^{(8)} &= -\frac{1}{2} V_2 Q^{(4)} Q^{(4)} + \frac{1}{3!} C_3 Q^{(2)} Q^{(2)} Q^{(2)} \\ &\quad + \frac{1}{4!} V_4 Q^{(2)} Q^{(2)} Q^{(2)} Q^{(2)}. \end{aligned}$$

Now, adding indices for internal coordinates and sums over them, we can get explicit formulas for the terms in effective rotational energy. The terms of the second order in effective rotational are analogous to the rigid body rotational energy:

$$h^{(2)}(\mathbf{J}) = \frac{1}{2}(\mathbf{J}, \Gamma^{-1}(q_0)\mathbf{J}). \quad (18)$$

For the terms of fourth order we obtain

$$h^{(4)}(\mathbf{J}) = -\frac{1}{8}(V_2^{-1})_{kl} \left( \mathbf{J}, \frac{\partial \Gamma^{-1}}{\partial q_k} \mathbf{J} \right) \left( \mathbf{J}, \frac{\partial \Gamma^{-1}}{\partial q_l} \mathbf{J} \right). \quad (19)$$

For the case of the Eckart frame this result was obtained by Montaldi and Roberts [12]. To calculate these terms it is necessary to know the matrix  $V_2$  of second derivatives of adiabatic potential in equilibrium configuration. The terms of sixth order require also the third derivatives of potential:

$$h^{(6)}(\mathbf{J}) = \frac{1}{2 \times 8} (V_2^{-1})_{km} (V_2^{-1})_{ln} \left( \mathbf{J}, \frac{\partial^2 \mathbb{I}^{-1}}{\partial q_k \partial q_l} \mathbf{J} \right) \left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_m} \mathbf{J} \right) \\ \times \left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_n} \mathbf{J} \right) - \frac{1}{6 \times 8} \frac{\partial^3 V}{\partial q_k \partial q_l \partial q_m} (V_2^{-1})_{ku} (V_2^{-1})_{lv} \\ \times (V_2^{-1})_{mw} \left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_u} \mathbf{J} \right) \left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_v} \mathbf{J} \right) \left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_w} \mathbf{J} \right). \quad (20)$$

In Eqs. (19) and (20) all partial derivatives on  $q$  are evaluated at the equilibrium configuration  $q_0$  and also the sums over indices of internal coordinates are understood.

Equations (18)–(20) can be used to predict the qualitative picture of relative equilibria at low  $J$ . The examples of this are given in the work of Montaldi and Roberts [12] and another example concerning  $H_2X$  molecules is discussed below. It should be noted, however, that at high  $J$  the convergence of effective rotational energy expansion may be problematic. In this case the numerical calculation of effective rotational energy (without expansion) can be done [8,9].

### B. Comparison with the quantum approach

Now we turn to a comparison of Eqs. (19) and (20) with analogous expressions for the terms in effective rotational Hamiltonians. The derivation of effective rotational Hamiltonians is usually based on the following conventions [5,21]. The molecule-fixed frame is defined by Eckart conditions, and its axes in equilibrium configuration coincide with principal axes of inertia; also the normal coordinates are chosen as internal ones. The effective rotational Hamiltonians are received as a result of (vibrational) contact transformation in the form of power series in operators of angular-momentum components [22,5]. Then the procedure of second (rotational) contact transformation can be done [22,4], but since it does not affect the corresponding classical expressions it is not essential to the present consideration. For comparison we have chosen the work of Aliev and Watson [22] in which the explicit formulas for the terms of sixth order in effective rotational Hamiltonian are derived.

The conventions we noted above allow us to give more detailed expressions for the terms given by Eqs. (19) and (20). Since  $q_k$  are normal coordinates, the matrix  $V_2^{-1}$  is diagonal:

$$(V_2^{-1})_{kl} = \frac{1}{\lambda_k} \delta_{kl}. \quad (21)$$

For the derivatives of inverse inertia tensor we get the following expressions:

$$\left. \frac{\partial (\mathbb{I}^{-1})_{\alpha\beta}}{\partial q_k} \right|_0 = - \frac{a_k^{\alpha\beta}}{I_\alpha^0 I_\beta^0}, \quad (22)$$

$$\left. \frac{\partial^2 (\mathbb{I}^{-1})_{\alpha\beta}}{\partial q_k \partial q_l} \right|_0 = - \frac{1}{I_\alpha^0 I_\beta^0} \sum_m (\zeta_{lm}^\alpha \zeta_{km}^\beta + \zeta_{km}^\alpha \zeta_{lm}^\beta) \\ + \frac{3}{4} \frac{1}{I_\alpha^0 I_\beta^0} \sum_\gamma \frac{1}{I_\gamma^0} (a_k^{\alpha\gamma} a_l^{\gamma\beta} + a_l^{\alpha\gamma} a_k^{\gamma\beta}). \quad (23)$$

Here we use the following notation:  $I_\alpha^0$  are the general moments of inertia in equilibrium configuration,  $a_k^{\alpha\beta} = \partial \mathbb{I}_{\alpha\beta} / \partial q_k|_0$  the inertial derivatives, and  $\zeta_{kl}^\alpha$  the Coriolis coupling coefficients [5,21]. We derive Eqs. (22) and (23) in the Appendix.

Using Eqs. (21)–(23), we obtain the expressions for the fourth- and sixth-order terms in effective rotational energy through the coefficients  $\lambda_k$ ,  $I_\alpha^0$ ,  $a_k^{\alpha\beta}$ ,  $\zeta_{kl}^\alpha$ . For the terms of fourth order we obtain Wilson's result

$$h^{(4)}(\mathbf{J}) = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta, \quad (24)$$

where

$$\tau_{\alpha\beta\gamma\delta} = - \frac{1}{2 I_\alpha^0 I_\beta^0 I_\gamma^0 I_\delta^0} \sum_k \frac{a_k^{\alpha\beta} a_k^{\gamma\delta}}{\lambda_k} \quad (25)$$

is a Wilson-Howard tensor [6,4]. The terms of sixth order have the form

$$h^{(6)}(\mathbf{J}) = \frac{1}{8} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} \tau_{\alpha\beta\gamma\delta\epsilon\zeta} J_\alpha J_\beta J_\gamma J_\delta J_\epsilon J_\zeta, \quad (26)$$

where

$$\tau_{\alpha\beta\gamma\delta\epsilon\zeta} = \frac{1}{I_\alpha^0 I_\beta^0 I_\gamma^0 I_\delta^0 I_\epsilon^0 I_\zeta^0} \left[ \frac{3}{4} \sum_{lm\mu} \frac{a_l^{\alpha\mu} a_m^{\mu\beta} a_l^{\gamma\delta} a_m^{\epsilon\zeta}}{\lambda_l \lambda_m I_\mu^0} \right. \\ \left. - \sum_{lmn} \frac{\zeta_{ln}^\alpha \zeta_{mn}^\beta a_l^{\gamma\delta} a_m^{\epsilon\zeta}}{\lambda_l \lambda_m} + \frac{1}{6} \sum_{lmn} \frac{k_{lmn} a_l^{\alpha\beta} a_m^{\gamma\delta} a_n^{\epsilon\zeta}}{\lambda_l \lambda_m \lambda_n} \right], \quad (27)$$

$$k_{lmn} = \left. \frac{\partial^3 V}{\partial q_l \partial q_m \partial q_n} \right|_0. \quad (28)$$

For comparison with the results of Ref. [22] it is also necessary to transfer to dimensionless normal coordinates, angular-momentum components in units of  $\hbar$  and energy in units of  $hc$  [5]. We find that there is an exact correspondence between Eqs. (24), (26) and corresponding quantum expressions, in which the operators of angular momentum are substituted by the corresponding classical variables. The split-

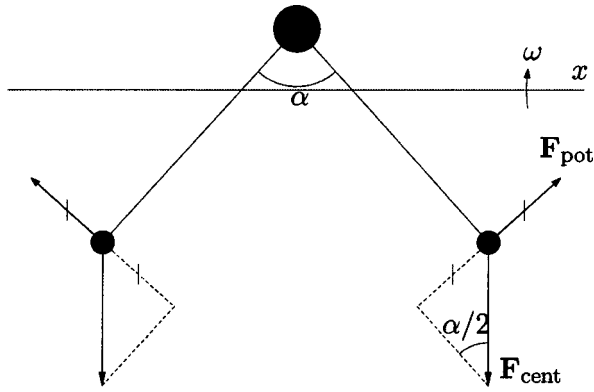


FIG. 1. Relative equilibria in the rigid bender model with the axis of rotation  $x$ . We consider the balance conditions only for the H nuclei since they imply the balance condition for the X nucleus.

ting of sixth-order terms in Ref. [22] into harmonic, Coriolis, and anharmonic parts corresponds exactly to our splitting in Eq. (27).

#### IV. RELATIVE EQUILIBRIA IN $H_2X$ MOLECULES

In this section we analyze the bifurcation in rotational dynamics of  $H_2X$  molecules. The simplest possible picture of this bifurcation is provided by the rigid bender model, which we discuss at first. Then we focus on the hypothetical molecule with accidental symmetric-top configuration and analyze the qualitative picture of relative equilibria in it at low  $J$  using Eq. (19). On the basis of these results we give the description of the bifurcation in the real  $H_2X$  molecules.

##### A. Rigid bender model

The rigid bender model, in which the  $X-H$  bonds are assumed to be “frozen” at their equilibrium distances, was used in many works for the qualitative description of rovibrational dynamics of  $H_2X$  molecules (see, e.g., Refs. [17,23,24]). In the work of Zhilinskii and Pavlichenkov [16] the rigid bender model was used to predict the bifurcation in the rotational dynamics of  $H_2X$  molecules.

In Ref. [16] the problem is analyzed using explicit equations of motion analogous to Eq. (1). An alternative approach we take here is based on the simple condition of balance for the potential, centrifugal, and reaction forces. Let  $M$  and  $m$  be the masses of  $X$  and  $H$ , respectively,  $l$  the equilibrium bond distance, and  $V_{rb}(\alpha)$  the potential function having the simplest form with one minimum point  $\alpha_0$ . (We assume at first that  $\alpha_0 > \pi/2$ .) Consider the relative equilibria with the axis of rotation  $x$  lying in the plane of a molecule perpendicular to the  $C_2$  symmetry axis. The presence of the constraints on the bonds implies that there are reaction forces, which we should take into account when considering the balance condition (see Fig. 1):

$$|\mathbf{F}_{cent}| \sin \frac{\alpha}{2} = |\mathbf{F}_{pot}|, \quad (29)$$

where

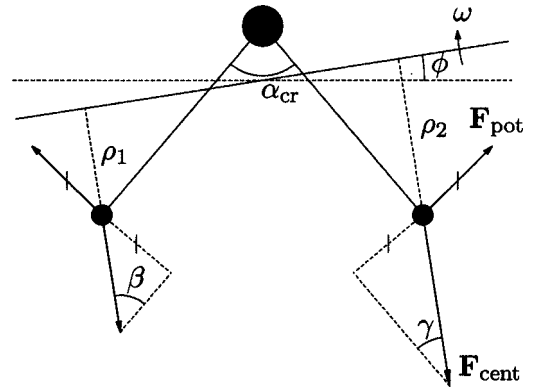


FIG. 2. Relative equilibria in the rigid bender model corresponding to accidental symmetric-top configuration. Here  $\beta = \alpha_{cr}/2 + \phi$  and  $\gamma = \alpha_{cr}/2 - \phi$ .

$$|\mathbf{F}_{cent}| = \frac{mM}{M+2m} \omega^2 l \cos \frac{\alpha}{2}, \quad |\mathbf{F}_{pot}| = -\frac{1}{l} \frac{\partial V_{rb}}{\partial \alpha}. \quad (30)$$

Condition (29) can be written also as

$$\frac{\partial}{\partial \alpha} \left( V_{rb} - \frac{I_x \omega^2}{2} \right) = 0, \quad \frac{\partial}{\partial \alpha} \left( V_{rb} + \frac{J^2}{2I_x} \right) = 0, \quad (31)$$

where  $I_x(\alpha)$  is the general moment of inertia corresponding to axis  $x$ . These equations describe a decrease of the angle  $\alpha$  of relative equilibrium configuration with an increase of angular momentum  $J$  or angular velocity  $\omega$ . The analogous conditions can be obtained for the rotation axes  $y$  (coinciding with the  $C_2$  axis) and  $z$  (perpendicular to the plane of a molecule).

Let us recall that only the principal axes of inertia can be the axes of rotation of relative equilibria. (This can be seen as a consequence of the conservation of angular momentum vector in space-fixed frame.) The axes  $x, y, z$  are the only principal axes of inertia in a generic case, but when the bond angle equals  $\alpha_{cr} = \arccos[m/(m+M)] < \pi/2$  the general moments of inertia  $I_x$  and  $I_y$  coincide and the molecule becomes an accidental symmetric top. In this case every axis in the plane of a molecule going through the center of mass becomes a principal axis of inertia.

To obtain the full picture of relative equilibria in the rigid bender model it is necessary to consider this accidental symmetric-top configuration with the axis of rotation lying in the plane of a molecule. Let  $\phi$  be the angle between the rotation axis and axis  $x$ . Let us assume that  $\phi < \alpha_{cr}/2$ . Analyzing the balance conditions for the two H nuclei we find that they are equivalent due to the identity

$$\rho_1 \sin \left( \frac{\alpha_{cr}}{2} + \phi \right) = \rho_2 \sin \left( \frac{\alpha_{cr}}{2} - \phi \right), \quad (32)$$

where  $\rho_1$  and  $\rho_2$  are distances from the two H nuclei to the axis of rotation (see Fig. 2). The proof of this identity is straightforward: it is necessary to calculate the distances  $\rho_1$  and  $\rho_2$  as functions of angle  $\phi$  and to use standard trigonometric formulas. Thus we see that every axis with  $\phi < \alpha_{cr}/2$  defines a relative equilibrium with certain  $J$ . The

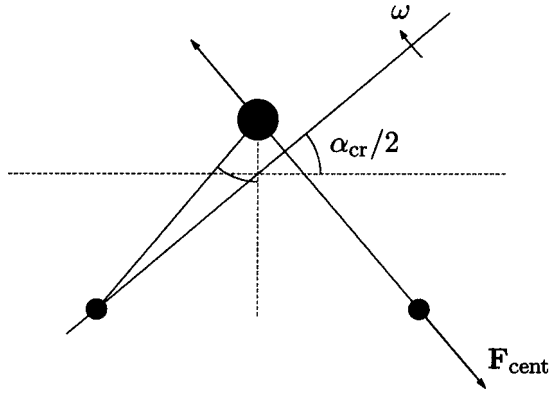


FIG. 3. Axis of rotation with  $\phi = \alpha_{\text{cr}}/2$  in a hypothetical molecule with accidental symmetric top configuration.

value  $\phi = 0$  corresponds to the critical value of angular momentum  $J_{\text{cr}}$ , which can be found from the condition

$$\left. \frac{\partial}{\partial \alpha} \left( V_{\text{rb}} + \frac{J_{\text{cr}}^2}{2I_x} \right) \right|_{\alpha_{\text{cr}}} = 0. \quad (33)$$

The angle  $\phi$  increases with  $J$  and at high  $J$  it approaches  $\alpha_{\text{cr}}/2$ . The equation describing this dependence can be written in the form [cf. Eq. (6)]

$$\left. \frac{\partial}{\partial \alpha} \left( V_{\text{rb}} + \cos^2 \phi \frac{J^2}{2I_x} + \sin^2 \phi \frac{J^2}{2I_y} \right) \right|_{\alpha_{\text{cr}}} = 0. \quad (34)$$

Thus we obtain the description of bifurcation in rotational dynamics: the number of relative equilibria changes at  $J_{\text{cr}}$  due to the appearance of two new axes of rotation, corresponding to accidental symmetric-top configuration [16].

The peculiarity of accidental symmetric-top configuration becomes more clear if we consider the rotation axis with  $\phi = \alpha_{\text{cr}}/2$ . This axis goes through the position of one H nucleus and is perpendicular to X-H bond with another H nucleus (see Fig. 3). In the hypothetical molecule in which the equilibrium bond angle  $\alpha_0$  equals  $\alpha_{\text{cr}}$  this axis corresponds to relative equilibria with arbitrary  $J$  since all centrifugal forces will be balanced by the reaction forces. We can interpret this as an appearance of bifurcation at  $J_{\text{cr}} = 0$ . When the equilibrium bond angle  $\alpha_0$  differs from  $\alpha_{\text{cr}}$  the bifurcation occurs at some  $J_{\text{cr}} > 0$ . To prove this the case  $\alpha_0 < \alpha_{\text{cr}}$  should also be considered. This can be done in a similar way; we only note that in this case the roles of the axes  $x$  and  $y$  are interchanged.

### B. A hypothetical molecule with accidental symmetric-top configuration

A hypothetical molecule with accidental symmetric-top configuration gives the simplest example of bifurcation in the rigid bender model, and the reaction forces play an important role in this case. It is very interesting whether the bifurcation in such a hypothetical molecule remains if we take off the constraints on the bonds. For the analysis of this problem we apply the method of effective rotational energy.

To do this we should first choose the molecule-fixed frame and internal coordinates. We use the Eckart frame and express the nuclear position vectors in this frame as linear combinations of the internal coordinates  $q_k$ :

$$R_{ai} = R_{ai}^0 + \frac{1}{\sqrt{m_i}} \sum_k l_{ai}^{(k)} q_k, \quad (35)$$

where the constants  $l_{ai}^{(k)}$  satisfy the equations, originating from the Eckart conditions, and also the orthogonality condition [see Eqs. (11)–(13) in Ref. [21]]. Usually the coordinates  $q_k$  are chosen to be the normal coordinates, but in our case the latter depend on the force constants due to the presence of two fully symmetrical modes. This is not very convenient and instead we use the following definition. We choose the internal coordinate  $q_1$  as corresponding to the “breathing” mode. Another fully symmetrical internal coordinate  $q_2$  (bending one) is then defined by the orthogonality condition; the asymmetrical coordinate  $q_3$  is defined uniquely up to a sign. The calculation gives the following expressions for the coefficients  $l_{ai}^{(k)}$ :

$$l^{(1)} = \begin{pmatrix} -P & P & 0 \\ -Q & -Q & R \\ 0 & 0 & 0 \end{pmatrix}, \quad (36a)$$

$$l^{(2)} = \begin{pmatrix} -P & P & 0 \\ Q & Q & -R \\ 0 & 0 & 0 \end{pmatrix}, \quad (36b)$$

$$l^{(3)} = \begin{pmatrix} Q & Q & -R \\ P & -P & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (36c)$$

where

$$P = \frac{1}{2}, \quad Q = \frac{1}{2} \sqrt{\frac{M}{M+2m}}, \quad R = \sqrt{\frac{m}{M+2m}}. \quad (37)$$

The first two columns in these matrices correspond to the displacements of H nuclei and the third to the displacements of X nucleus. The simplicity of these expressions is another surprising peculiarity of symmetric-top configuration, since for the general value of bending angle  $\alpha_0$  they are much more complicated. The relationship between these three displacements can be seen if we plot the corresponding vectors at one graphic (see Fig. 4).

Using these definitions, we calculate the first derivatives of inverse inertia tensor in equilibrium configuration and use them to receive the following functions:

$$\left( \mathbf{J}, \frac{\partial \mathbf{I}^{-1}}{\partial q_1} \mathbf{J} \right) = -\tau \left( J_x^2 + J_y^2 + \frac{1}{2} J_z^2 \right), \quad (38a)$$

$$\left( \mathbf{J}, \frac{\partial \mathbf{I}^{-1}}{\partial q_2} \mathbf{J} \right) = \tau (J_x^2 - J_y^2), \quad (38b)$$

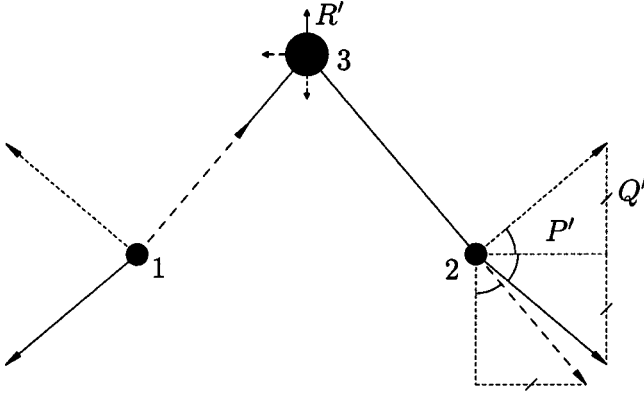


FIG. 4. Vibrational displacements in accidental symmetric-top configuration. Here  $P' = P/\sqrt{m}$ ,  $Q' = Q/\sqrt{m}$ ,  $R' = R/\sqrt{M}$  [see Eqs. (35)–(37)].

$$\left( \mathbf{J}, \frac{\partial \mathbb{I}^{-1}}{\partial q_3} \mathbf{J} \right) = -2\tau J_x J_y, \quad (38c)$$

where  $\tau = (\sqrt{2}/l^3)[(M+m)/Mm]^{3/2}$ . Note that there is an evident resemblance between Eqs. (38a)–(38c) and analogous expressions, obtained for equilateral  $X_3$  molecule by Montaldi and Roberts [12]. This is because the  $X_3$  molecule is in fact a special case of our consideration (with  $M = m$ ).

The inverse matrix of second derivatives of potential in equilibrium configuration in chosen coordinates  $q_k$  has the general form

$$V_2^{-1} = \begin{pmatrix} K_1 & K_{12} & 0 \\ K_{12} & K_2 & 0 \\ 0 & 0 & K_3 \end{pmatrix}, \quad (39)$$

where the coefficient  $K_{12}$  corresponds to the mixing of the breathing and bending modes.

Using Eqs. (19), (38), and (39), we obtain the following expression for the terms of fourth order in effective rotational energy:

$$h^{(4)}(\mathbf{J}) = -\frac{1}{8}\tau^2 [K_1(J_x^2 + J_y^2 + \frac{1}{2}J_z^2)^2 - 2K_{12}(J_x^2 + J_y^2 + \frac{1}{2}J_z^2) \times (J_x^2 - J_y^2) + K_2(J_x^2 - J_y^2)^2 + 4K_3J_x^2J_y^2]. \quad (40)$$

To answer the question about the bifurcation in the hypothetical molecule it is sufficient to consider the values of effective rotational energy only for the vectors  $\mathbf{J}$  lying in the plane  $xy$ :

$$E_J(\phi) = h(J \cos \phi, J \sin \phi, 0). \quad (41)$$

The terms of second order bring only the scalar part in  $E_J(\phi)$ . From Eq. (40) we obtain

$$E_J^{(4)}(\phi) = \frac{1}{8}\tau^2 J^4 p(\cos^2 \phi), \quad (42)$$

where

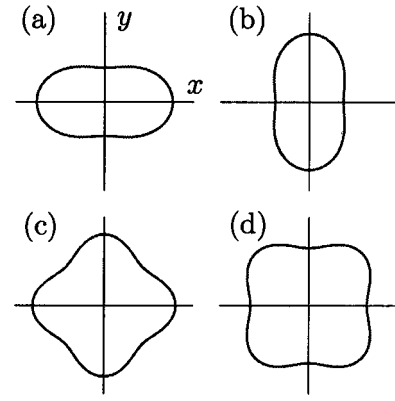


FIG. 5. Typical radial plots of functions  $E_J(\phi)$  at low  $J$ : (a)  $|\lambda| \geq 1$  (or  $K_2 = K_3$ ),  $K_{12} > 0$ ; (b)  $|\lambda| \geq 1$  (or  $K_2 = K_3$ ),  $K_{12} < 0$ ; (c)  $|\lambda| < 1$ ,  $K_2 < K_3$ ; (d)  $|\lambda| < 1$ ,  $K_2 > K_3$ .

$$p(x) = 4(K_3 - K_2)x^2 + 4(K_{12} + K_2 - K_3)x - K_1 - K_2 - 2K_{12}. \quad (43)$$

The behavior of the quadratic function  $p(x)$  in the interval  $[0, 1]$  defines the qualitative picture of relative equilibria at low  $J$ . Obviously, there are four typical situations, which are plotted in Fig. 5. The appearance of bifurcation depends on the following parameter:

$$\lambda = \frac{K_{12}}{K_2 - K_3}. \quad (44)$$

Provided  $|\lambda| < 1$  four additional stationary points appear with the angle  $\phi$ , defined by the equation

$$\cos^2 \phi = \frac{1}{2}(1 + \lambda). \quad (45)$$

The type of these points is defined by the relationship between  $K_2$  and  $K_3$ : in the case  $K_2 < K_3$  they are minima, and in the case  $K_2 > K_3$  maxima.

Note that minima of function  $E_J$  correspond to the saddle points of function  $h_J$  (defined on the whole sphere), and maxima of  $E_J$  correspond to maxima of  $h_J$ . (This is because the stationary points of  $h_J$  lying on axis  $z$  are minima as seen from the second-order terms.)

There is also the case, when  $K_2 = K_3$  and  $K_{12} = 0$ . In this case the terms of fourth order give no information on relative equilibria we are interested in and the terms of sixth order should be considered. Such a situation is realized in equilateral  $X_3$  molecule (see Ref. [12]).

### C. Comparison with the rigid bender model

Let us compare the results obtained above with the rigid bender model. This model can be considered as a limit case, corresponding to infinitely rigid bonds. To describe this, we define a family of potentials

$$V(\alpha, l_1, l_2) = V_{\text{rb}}(\alpha) + \frac{N_l}{2}(l_1 - l)^2 + \frac{N_l}{2}(l_2 - l)^2, \quad (46)$$

where  $l_1, l_2$  are the bond distances and the parameter  $N_l$  defines the rigidity of the bonds. The rigid bender model corresponds to the limit  $N_l \rightarrow \infty$  [25].

The matrix of second derivatives of the potential given by Eq. (46) in coordinates  $q_1, q_2, q_3$  has the form

$$V_2 = \begin{pmatrix} k_1 & k_{12} & 0 \\ k_{12} & k_2 & 0 \\ 0 & 0 & k_3 \end{pmatrix}, \quad (47)$$

where

$$k_1 = (1 + \xi) \frac{N_l}{m}, \quad k_{12} = -\xi \frac{N_l}{m}, \quad k_3 = \frac{1 + 2\xi}{1 + \xi} \frac{N_l}{m},$$

$$k_2 = \frac{\xi^2}{1 + \xi} \frac{N_l}{m} + \frac{1 + 2\xi}{1 + \xi} \frac{N_\alpha}{m}, \quad (48)$$

$$\xi = \frac{m}{M}, \quad N_\alpha = \frac{2}{l^2} \frac{\partial^2 V_{\text{rb}}}{\partial \alpha^2} \Big|_{\alpha_{\text{cr}}}. \quad (49)$$

Inverting this matrix we find

$$\lambda = \frac{\xi}{1 + \xi} \left( 1 - \frac{N_\alpha}{N_l} \right)^{-1}, \quad (50)$$

$$K_2 - K_3 = \frac{1 + \xi}{1 + 2\xi} \frac{m}{N_\alpha} \left( 1 - \frac{N_\alpha}{N_l} \right). \quad (51)$$

In the limit  $N_l \rightarrow \infty$  we have  $\lambda \rightarrow m/(M+m)$  and also  $K_2 - K_3 > 0$ , which corresponds to case (d) in Fig. 5. From Eq. (45) we find that the angle  $\phi$  at which the maxima appear tends to  $\alpha_{\text{cr}}/2$ . Thus we have the full correspondence with the rigid bender model.

The potential in the form given by Eq. (46) provides a good approximation to the quadratic form of potential in the real  $\text{H}_2\text{X}$  molecules. Therefore, we consider also the case of finite  $N_l$ . From Eqs. (50) and (51) we find that  $|\lambda| < 1$  and  $K_2 > K_3$  provided

$$N_l > \frac{M+m}{M} N_\alpha. \quad (52)$$

This condition gives the lower bound for the rigidity of bonds at which the qualitative features of the rigid bender model remain.

The physical meaning of condition (52) becomes more clear if we consider the frequencies of normal vibrations  $\omega_k$  instead of  $N_l$  and  $N_\alpha$ . The eigenvalues of the matrix  $V_2$  given by Eq. (47) are exactly the squares of frequencies (since  $q_k$  are mass-weighted coordinates). Expanding  $m\omega_k^2$  in powers of parameter  $\xi = m/M$ , we obtain

$$m\omega_1^2 = N_l + N_l \xi + O(\xi^2), \quad (53a)$$

$$m\omega_2^2 = N_\alpha + N_\alpha \xi + O(\xi^2), \quad (53b)$$

$$m\omega_3^2 = N_l + N_l \xi + O(\xi^2). \quad (53c)$$

Therefore, in the limit  $M \gg m$ , condition (52) becomes simply

$$\omega_{\text{stretching}} > \omega_{\text{bending}}, \quad (54)$$

or, more exactly,

$$\omega_{1(3)}^2 > \omega_2^2 (1 + \xi) + O(\xi^2). \quad (55)$$

In the rigid bender model the additional relative equilibria correspond to accidental symmetric-top configuration. When the constraints are taken off the situation gets different. From Eqs. (16), (38), and (39) we have

$$Q_3^{(2)}(\mathbf{J}) = \tau K_3 J_x J_y. \quad (56)$$

Therefore, in additional relative equilibria the bonds X-H have different length. For the axis with  $\phi > 0$  we have  $J_x > 0$ ,  $J_y > 0$ , and  $Q_3^{(2)} > 0$ , which means that the right bond X-H will be larger than the left (see Fig. 4). For the axis with  $\phi < 0$  the situation is inverted.

#### D. Bifurcation in real molecules

In the real  $\text{H}_2\text{X}$  molecules the equilibrium bond angle  $\alpha_0$  is larger than  $\alpha_{\text{cr}}$ . The difference  $\alpha_0 - \alpha_{\text{cr}}$  decreases in the sequence  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$ , and for  $\text{H}_2\text{Te}$  molecule it is very small (less than  $1^\circ$ ) [26]. To analyze the picture of relative equilibria in these molecules at small  $J$  we use the exact terms of second order in effective rotational energy and the terms of fourth order defined as if in hypothetical molecule.

Using this assumption we can write

$$E_J(\phi) = (A \cos^2 \phi + B \sin^2 \phi) J^2 + E_J^{(4)}(\phi) + \dots, \quad (57)$$

where  $A$  and  $B$  are rotational constants and the fourth-order terms are given by Eq. (42). As in the case of hypothetical molecule the problem reduces to the analysis of the behavior of quadratic function in the interval  $[0, 1]$ :

$$E_J(\phi) = E_0(J^2) + \tau^2 (K_2 - K_3) J^4 p_J(\cos^2 \phi) + \dots, \quad (58)$$

$$p_J(x) = -\frac{1}{2} x^2 + \frac{1}{2} (1 + \lambda) x + \frac{\delta}{J^2} x, \quad (59)$$

where

$$\delta = \frac{A - B}{\tau^2 (K_2 - K_3)}. \quad (60)$$



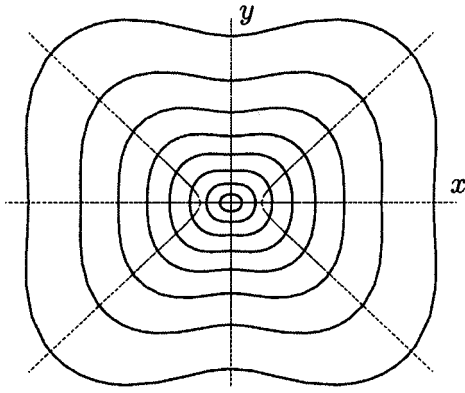


FIG. 6. Radial plots of functions  $E_J(\phi)$  at different  $J$  showing the bifurcation. Dashed lines correspond to stationary points of  $E_J(\phi)$ .

In the real  $H_2X$  molecules  $A$  is slightly larger than  $B$ , and we also assume that  $|\lambda| < 1$ ,  $K_2 > K_3$  [since in all  $H_2X$  molecules inequality (54) holds]. The qualitative picture of functions  $E_J(\phi)$  is shown in Fig. 6. For the critical value  $J_{cr}$  we get the following estimate:

$$J_{cr}^2 = \frac{2\delta}{1-\lambda}. \quad (61)$$

Also we obtain the approximate formula for the angle  $\phi$  describing the position of maxima [cf. Eq. (45)]:

$$\cos^2 \phi = \frac{1}{2}(1+\lambda) + \frac{\delta}{J^2}. \quad (62)$$

This qualitative picture agrees with the results of numerical calculations [9,18]. The appearance of four maxima of function  $E_J(\phi)$  [and, consequently, of function  $h_J(\theta, \phi)$ ] at  $J > J_{cr}$  explains the formation of fourfold clusters in the upper part of rotational multiplets [15,17].

The most important parameter of bifurcation is the critical value of angular momentum  $J_{cr}$ . The rigid bender model gives the following estimate [15,26]:

$$J_{cr}^{(rb)} = \frac{\omega_2}{4A} \sqrt{\frac{A-B}{C}}. \quad (63)$$

It is interesting to compare this result with Eq. (61). To do this we consider the limit  $M \gg m$  in Eq. (61). Since  $\alpha_0$  is close to  $\alpha_{cr}$  we may assume that the relationship between the parameters needed is as in the hypothetical molecule. Using Eqs. (50), (51), (53), and an approximate relation  $A \approx 2C \approx 1/2ml^2$ , we find

$$J_{cr} = \frac{1}{\sqrt{1 - \frac{\omega_2^2}{\omega_{1(3)}^2}}} J_{cr}^{(rb)}. \quad (64)$$

Since in  $H_2X$  molecules the ratio  $\omega_{1(3)}/\omega_2$  is about 2.3, the value  $J_{cr}$  will be  $\approx 10\%$  higher than  $J_{cr}^{(rb)}$ . This result agrees with the known critical values of angular momentum: 18.9 (16.9) for  $H_2S$ , 12.5 (11.4) for  $H_2Se$ , and 9.3 (8.5) for  $H_2Te$  (values in parentheses correspond to the rigid bender model) [18].

The  $H_2O$  molecule is a special case in the sequence of  $H_2X$  molecules. The equilibrium bond angle  $\alpha_0$  in this molecule is sufficiently larger than  $\alpha_{cr}$  and this results in a comparatively high value of  $J_{cr}$  (35.2) [18]. The main peculiarity in this molecule is the presence of inverse bifurcation at  $J > 50$  [9,18,27]. This inverse bifurcation explains the absence of fourfold clusters in  $H_2O$  molecule. The analytical description of this bifurcation seems to be difficult due to high values of angular momentum involved.

## V. CONCLUSION

In this paper we have discussed the method of effective rotational energy which traces back to the work of Wilson [6]. We have shown that this method has a natural interpretation in terms of relative equilibria in molecules. We derived the explicit formulas for the terms in effective rotational energy up to sixth order in angular-momentum components and found that they are in accordance with the analogous expressions for effective rotational Hamiltonians. As an application we have considered the problem of bifurcation in rotational dynamics of  $H_2X$  molecules. We have shown that in the rigid bender model this bifurcation can be described using the balance conditions for the potential, centrifugal, and reaction forces. We found also that the method of effective rotational energy allows us to give the analytical description of the bifurcation without the suggestion of constant bond length.

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## APPENDIX

In this appendix we derive Eqs. (22) and (23) using the notation and identities from the work of Watson [21]. First we note that it is possible to express the derivatives of inverse inertia tensor through the derivatives of inertia tensor:

$$\frac{\partial \mathbb{I}^{-1}}{\partial q_k} = -\mathbb{I}^{-1} \frac{\partial \mathbb{I}}{\partial q_k} \mathbb{I}^{-1}, \quad (A1)$$

$$\begin{aligned} \frac{\partial^2 \mathbb{I}^{-1}}{\partial q_k \partial q_l} = & -\mathbb{I}^{-1} \frac{\partial^2 \mathbb{I}}{\partial q_k \partial q_l} \mathbb{I}^{-1} + \mathbb{I}^{-1} \frac{\partial \mathbb{I}}{\partial q_k} \mathbb{I}^{-1} \frac{\partial \mathbb{I}}{\partial q_l} \mathbb{I}^{-1} \\ & + \mathbb{I}^{-1} \frac{\partial \mathbb{I}}{\partial q_l} \mathbb{I}^{-1} \frac{\partial \mathbb{I}}{\partial q_k} \mathbb{I}^{-1}. \end{aligned} \quad (A2)$$

Using Eq. (A1) and the definition of coefficients  $a_k^{\alpha\beta}$ , we obtain Eq. (22). To prove Eq. (23) we need an explicit formula for the second derivatives of inertia tensor. By the definition of inertia tensor, we have

$$\left. \frac{\partial^2 \mathbb{I}_{\alpha\beta}}{\partial q_k \partial q_l} \right|_0 = 2 \delta_{\alpha\beta} \sum_{\gamma i} l_{\gamma i, k} l_{\gamma i, l} - \sum_i (l_{\alpha i, k} l_{\beta i, l} + l_{\alpha i, l} l_{\beta i, k}). \quad (\text{A3})$$

Next we use the orthogonality condition for the coefficients  $l_{\alpha i, k}$ ,

$$\sum_{\alpha i} l_{\alpha i, k} l_{\alpha i, l} = \delta_{kl} \quad (\text{A4})$$

and the sum rule

$$\sum_m \zeta_{km}^{\alpha} \zeta_{lm}^{\beta} = \delta_{\alpha\beta} \delta_{kl} - \sum_i l_{\alpha i, l} l_{\beta i, k} - \frac{1}{4} \sum_{\gamma} a_k^{\alpha\gamma} \frac{1}{I_{\gamma}^0} a_l^{\gamma\beta}. \quad (\text{A5})$$

Using Eqs. (A2)–(A5), we obtain Eq. (23). It is interesting to note that the second term in the right-hand side of Eq. (23) is exactly  $(\partial^2 \mu_{\alpha\beta} / \partial q_k \partial q_l)|_0$  as follows from Eq. (31) in Ref. [5].

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