



ELSEVIER

5 March 1999

Chemical Physics Letters 301 (1999) 435–440

**CHEMICAL
PHYSICS
LETTERS**

Shape-phase transitions in the vibron model and bent molecules

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Received 2 December 1998; in final form 18 December 1998

Abstract

A mean field study of triatomic molecules in the vibron model is carried out. Analytical solutions for the mean fields are found, and shape-phase transitions in the model are investigated utilizing these solutions. The Majorana interactions are shown to play an essential role in driving the phase transition from linear to bent shape. Results presented here will facilitate realistic studies of bent molecules within the symmetry-breaking approach. © 1999 Elsevier Science B.V. All rights reserved.

The vibron model [1–5] provides an algebraic framework for treating problems in molecular spectroscopy and has been especially useful in describing complex spectra of polyatomic molecules (see Ref. [6] for a recent review of the model and Ref. [7] for a pedagogical introduction to the group theory involved). The basic building blocks of the model are the scalar s and vector p bosons, the latter representing the dipole degree of freedom in a molecular bond while the former is needed to generate a finite, anharmonic, spectrum. The bilinear products of the boson creation and annihilation operators generate the $U(4)$ algebra which describes the dynamics of the system. The vibron model is extended to polyatomic molecules by introducing a set of boson operators $\{s_i, p_{i\mu}\}$ for each molecular bond i , and the dynamics of the coupled system is described by the product algebra $U_1 \otimes U_2 \otimes \dots$. There are two basic classes of dynamical symmetries of the model: (i) $O(4)$

limits associated with rotational spectra, and (ii) $U(3)$ limits associated with vibrational spectra. The former provides an analytically solvable zeroth-order approximation for molecular rotation–vibration spectra and, therefore, has been the focus of developments. This zeroth-order description can be improved by including either higher-order interactions formed exclusively from the $O(4)$ generators in the Hamiltonian, which preserve the $O(4)$ symmetry, or interactions formed from the $U(3)$ generators, which break it. The latter approach normally requires numerical diagonalization, while the former has the advantage of analytical formulation and, therefore, it has been used almost exclusively in practical applications of the vibron model.

A geometrical interpretation of the vibron model in terms of the bond lengths and angles can be provided using the mean field techniques [8–14]. An extension of the formalism to finite temperatures and discussion of the resulting phase space transitions in excited triatomic molecules was given in Ref. [15]. The general mean field formalism for triatomic molecules was developed in Refs. [12–14], where it

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was pointed out that the dynamical symmetry limits of the model are restricted to a description of linear molecules, and one has to break the symmetries to obtain a geometrically correct bent molecule. Due to the complexity of the results, a general investigation of shape-phase transitions in the vibron model was not performed in these studies. Rather, a numerical mean field analysis of the water molecule was presented in Ref. [14] as a specific example of bent molecules. Unfortunately, as an independent investigation of the results shows, the numerical fit obtained in Ref. [14] appears to correspond to a runaway solution, nothing to do with the actual properties of the water molecule.¹ Clearly, a mean field study of the shape-phase transitions in triatomic molecules, depicting the critical points in a phase diagram of parameters, would provide a valuable guide in searches for realistic description of bent molecules. An intuitive understanding of the role each parameter plays in the shape transition would help avoid the pitfalls encountered in multiple-parameter fit situations.

In a recent detailed study using the analytical $1/N$ expansion method, the symmetry breaking approach was shown to provide a viable description of diatomic molecules [17,18]. Extension of the $1/N$ expansion to triatomic molecules requires prior knowledge of the shape of the molecule for angular momentum projection purposes; thus, it gives another incentive for such a study.

The purpose of this Letter is to present a mean field study of the shape-phase transitions in triatomic molecules using a general Hamiltonian with one- and two-body terms

$$H = H_1 + H_2 + H_{12}. \quad (1)$$

where H_i , $i = 1, 2$, represent the individual bonds

$$H_i = -\kappa_i \hat{D}_i \cdot \hat{D}_i + \kappa'_i \hat{L}_i \cdot \hat{L}_i + \varepsilon_i \hat{n}_{p_i} + \sigma_i \hat{n}_{p_i}^2, \quad (2)$$

¹ The equilibrium mean fields given in Ref. [14] do not satisfy the extremum conditions. Further, the Hamiltonian parameters found in the fit are two orders of magnitude larger than the typical values used in the literature [16], and as a numerical diagonalization of the Hamiltonian shows, they lead to a similarly inflated spectrum compared to the experimental spectrum of water.

and H_{12} , the interaction between the two bonds

$$H_{12} = -\kappa_{12} \hat{D}_1 \cdot \hat{D}_2 + \kappa'_{12} \hat{L}_1 \cdot \hat{L}_2 + \sigma_{12} \hat{n}_{p_1} \hat{n}_{p_2} + \lambda_4 M_4 + \lambda_3 M_3. \quad (3)$$

The dipole, angular momentum and the p -boson number operators in (2) are defined, respectively, by

$$\hat{D}_\mu = [s^\dagger \tilde{p} + p^\dagger \tilde{s}]_\mu^{(1)}, \quad \hat{L}_\mu = -\sqrt{2} [p^\dagger \tilde{p}]_\mu^{(1)},$$

$$\hat{n}_p = \sum_\mu p_\mu^\dagger p_\mu, \quad (4)$$

where brackets denote tensor coupling and tilde, $\tilde{b}_{lm} = (-1)^m b_{l-m}$. M_3 and M_4 in (3) are the Majorana operators of the combined groups $U_{12}(3)$, and $U_{12}(4)$, defined by

$$M_3 = 2 [p_1^\dagger p_2^\dagger]^{(1)} \cdot [\tilde{p}_2 \tilde{p}_1]^{(1)},$$

$$M_4 = (s_1^\dagger p_2^\dagger - s_2^\dagger p_1^\dagger) \cdot (\tilde{p}_2 s_1 - \tilde{p}_1 s_2) + M_3. \quad (5)$$

The \hat{n}_p terms and M_3 in Eqs. (2) and (3) belong to the $U(3)$ algebras and are, thus, responsible for breaking the $O(4)$ symmetry. The Hamiltonian parameters are determined from fits to spectra [6], according to which the dipole interactions dominate and are attractive (hence the negative signs for κ_i and κ_{12} above). Study of the rotational expansion of vibrational bands in diatomic molecules indicates that the strength of the ε and σ terms should be limited to a perturbative range compared to the dipole interactions [17,18]. Otherwise, the rotational spectra obtained in the model exhibit large deviations from the experimentally observed ones.

The ground state of the combined boson system is given by a product of individual condensates

$$|N_1, N_2, r_1, r_2\rangle = (N_1! N_2!)^{-1/2} (b_1^\dagger)^{N_1} (b_2^\dagger)^{N_2} |0\rangle. \quad (6)$$

Aligning the first bond along the z axis and rotating the second one in the $x-z$ plane, the intrinsic bosons can be written as

$$b_1^\dagger = (1 + r_1^2)^{-1/2} (s_1^\dagger + r_1 p_{10}^\dagger),$$

$$b_2^\dagger = (1 + r_2^2)^{-1/2} \left\{ s_2^\dagger + r_2 [\cos \theta p_{20}^\dagger + \sin \theta (p_{2-1}^\dagger - p_{21}^\dagger) / \sqrt{2}] \right\}. \quad (7)$$

Here the mean fields r_1 and r_2 are associated with the bond lengths and θ is related to the bond angle θ_b by $\theta = \pi - \theta_b$. The range of r_i is $[0, \infty]$, and θ is $[0, \pi/2]$ (from the usual range of θ_b , $[\pi/2, \pi]$ for XYZ and XY_2 molecules). The energy surface follows from the expectation value of the Hamiltonian (1) in the condensate (6), and, in the large N limit, is given by

$$\begin{aligned}
 E(r_1, r_2, \theta) &= \sum_{i=1}^2 \left(\frac{N_i r_i}{1 + r_i^2} \right)^2 \left[-4\kappa_i + \varepsilon'_i (1 + r_i^2) \right. \\
 &\quad \left. + \sigma_i r_i^2 \right] + \frac{N_1 N_2}{(1 + r_1^2)(1 + r_2^2)} \left[\lambda_4 (r_1^2 + r_2^2) \right. \\
 &\quad \left. + \sigma_{12} r_1^2 r_2^2 - 2v r_1 r_2 \cos \theta + \lambda r_1^2 r_2^2 \sin^2 \theta \right], \quad (8)
 \end{aligned}$$

where we have introduced

$$\varepsilon'_i = \varepsilon_i / N_i, \quad v = (2\kappa_{12} + \lambda_4), \quad \lambda = \lambda_3 + \lambda_4. \quad (9)$$

The extremum conditions on (8) lead to a set of three coupled non-linear equations, which appear rather complicated, so that no attempt has been made for analytical solutions. In the $1/N$ expansion study of diatomic molecules [17,18], it has been found that the variable

$$a = 2r^2 / (1 + r^2), \quad (10)$$

which corresponds to the ‘average angular momentum squared’ carried by an intrinsic boson, provides a much more convenient parametrization for the energy surface. It maps the infinite range of r monotonically onto $[0, 2]$ for a . Using the transformation $r_i \rightarrow a_i$ in Eq. (8), we find that the energy surface becomes

$$\begin{aligned}
 E(a_1, a_2, \theta) &= \sum_{i=1}^2 N_i^2 a_i \left[-\kappa_i (2 - a_i) + \varepsilon'_i / 2 \right. \\
 &\quad \left. + \sigma_i a_i / 4 \right] + N_1 N_2 / 4 \left[2\lambda_4 (a_1 + a_2 - a_1 a_2) \right. \\
 &\quad \left. + \sigma_{12} a_1 a_2 - 2v f_1 f_2 \cos \theta + \lambda a_1 a_2 \sin^2 \theta \right], \quad (11)
 \end{aligned}$$

where $f_i = [a_i(2 - a_i)]^{1/2}$. To find the extremum points, we set the derivatives of $E(a_1, a_2, \theta)$ w.r.t. a_1 , a_2 and θ to zero

$$\begin{aligned}
 N_1 \left[-4\kappa_1 (1 - a_1) + \varepsilon'_1 + \sigma_1 a_1 \right] + N_2 \left[\lambda_4 (1 - a_2) \right. \\
 \left. + \sigma_{12} a_2 / 2 - v (1 - a_1) (f_2 / f_1) \cos \theta \right. \\
 \left. + \lambda a_2 \sin^2 \theta / 2 \right] = 0, \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 N_2 \left[-4\kappa_2 (1 - a_2) + \varepsilon'_2 + \sigma_2 a_2 \right] + N_1 \left[\lambda_4 (1 - a_1) \right. \\
 \left. + \sigma_{12} a_1 / 2 - v (1 - a_2) (f_1 / f_2) \cos \theta \right. \\
 \left. + \lambda a_1 \sin^2 \theta / 2 \right] = 0, \quad (13)
 \end{aligned}$$

$$\sin \theta [v f_1 f_2 + \lambda a_1 a_2 \cos \theta] = 0. \quad (14)$$

Eq. (14) has three solutions for the variable θ , given by $\theta = 0, \pi$ and $\cos \theta = -(v f_1 f_2 / \lambda a_1 a_2)$. Substituting $\cos \theta$ in Eqs. (12) and (13), one gets two linear equations for a_1 and a_2 , so solutions for the bent shape can be readily obtained. For the linear shapes, obtained by substituting $\theta_1 = 0$ or π in (12) and (13), we find linear equations in a_1 and a_2 , save for the dependence on f_i . Thus, they can be solved iteratively in the spirit of the Hartree–Bose equations, starting with the initial values of $f_1 = f_2 = 1$, and updating them until a_1 and a_2 converge.

Rather than pursuing these still complicated solutions, we first consider the special case of symmetric XY_2 molecules, for which simple expressions for the mean fields can be obtained in all three cases. With the insight gained from XY_2 molecules, the study of shapes in the general case will become more transparent. Due to the symmetry of XY_2 molecules, $N_1 = N_2 = N$, $H_1 = H_2$, and we further set $a_1 = a_2 = a$, $\kappa_1 = \kappa_2 = \kappa$, etc. Since N is now just a scale parameter for the energies, we put $N = 1$ for convenience. Solution of Eqs. (12)–(14) then yields the following mean fields and the corresponding energies for the extremum points

$$\begin{aligned}
 \theta = 0, \quad a_0 = 1 - (\varepsilon' + \sigma') / (\omega + \sigma'), \\
 E_0 = -a_0 (\omega - \varepsilon') / 2, \quad (15)
 \end{aligned}$$

$$\begin{aligned}
 \theta = \pi, \quad a_\pi = 1 - (\varepsilon' + \sigma') / (\omega - 2v + \sigma'), \\
 E_\pi = -a_\pi (\omega - 2v - \varepsilon') / 2, \quad (16)
 \end{aligned}$$

$$\begin{aligned}
 \cos \theta = -v (g - g') / \lambda g', \quad a_\theta = 2g' / g, \\
 E_\theta = \frac{-1}{g} \left[(\omega - \varepsilon') (\omega - 2v - \varepsilon') \lambda \right. \\
 \left. - 2(\varepsilon' + \sigma') v^2 \right]. \quad (17)
 \end{aligned}$$

Here the two functions g and g' are defined as

$$g = \lambda^2 + 2(\omega - \nu + \sigma')\lambda + \nu^2, \\ g' = (\omega - \nu - \varepsilon')\lambda + \nu^2, \quad (18)$$

and we have introduced two new parameters for convenience

$$\sigma' = \sigma + \sigma_{12}/2, \quad \omega = 4\kappa + 2\kappa_{12}. \quad (19)$$

The physical significance of ω above is that the symmetric stretching energy is given by $N\omega$ to leading order in the $O_{12}(4)$ dynamical symmetries. Note that λ appears only in the bent solution and it will be seen to drive the shape-phase transition. To determine the nature of the extremum points we need to examine their second derivatives

$$\partial^2 E / \partial a^2|_0 = (\omega + \sigma'), \quad \partial^2 E / \partial \theta^2|_0 = a_0 g_1 / 2, \quad (20)$$

$$\partial^2 E / \partial a^2|_\pi = (\omega - 2\nu + \sigma'), \\ \partial^2 E / \partial \theta^2|_\pi = -a_\pi g_2 / 2, \quad (21)$$

$$\partial^2 E / \partial a^2|_\theta = \omega - \nu + \sigma' + \nu \cos \theta + \lambda \sin^2 \theta / 2, \\ \partial^2 E / \partial \theta^2|_\theta = -\lambda (a_\theta \sin \theta)^2 / 2, \\ \partial^2 E / \partial a \partial \theta|_\theta = -\nu \sin \theta, \quad (22)$$

where

$$g_1 = \nu + \lambda + (\varepsilon' + \sigma')(\nu - \lambda) / (\omega + \sigma'), \\ g_2 = \nu - \lambda + (\varepsilon' + \sigma')(\nu + \lambda) / (\omega - 2\nu + \sigma'). \quad (23)$$

The cross-derivatives vanish at 0 and π but not at θ , so we need the Hessian at θ as well

$$\left[(\partial^2 E / \partial a^2)(\partial^2 E / \partial \theta^2) - (\partial^2 E / \partial a \partial \theta)^2 \right]_\theta \\ = -g(a_\theta \sin \theta)^2 / 4. \quad (24)$$

Finally, the energy differences will be handy in finding the absolute minimum. After some algebraic manipulations, these can be written as

$$E_\pi - E_0 = \nu \left[1 - (\varepsilon' + \sigma')^2 / (\omega + \sigma')(\omega - 2\nu + \sigma') \right], \quad (25)$$

$$E_\theta - E_0 = (\omega + \sigma') g_1^2 / 2g, \quad (26)$$

$$E_\theta - E_\pi = (\omega - 2\nu + \sigma') g_2^2 / 2g, \quad (27)$$

In all of the above equations for XY_2 molecules, we have deliberately separated the ε' and σ' terms. As noted earlier these terms are limited to a perturbative range in realistic applications of the vibron model. Inspection of Eqs. (20) and (25) shows that E_0 is a minimum and lower than E_π provided $g_1 > 0$ and $\nu > 0$. From Eqs. (22) and (24), two essential conditions for the existence of a bent minimum are that $\lambda < 0$ and $g < 0$. These also ensure that E_θ is the absolute minimum since both energy differences in Eqs. (26) and (27) are negative ($g < 0$ only if $\omega - 2\nu + \sigma' > 0$ (see Eq. (29))).

In the light of these results, we can now unambiguously determine the range of parameters in Eq. (17) for which the bent mean fields have the desired ranges, i.e., $\pi/2 < \theta < 0$ and $0 < a_\theta < 2$. Inspection of Eq. (17) shows that, in addition to the above conditions, $g' < 0$, $g - g' < 0$ and $g_1 < 0$ are required. These inequalities are satisfied when λ is in the range $\lambda_{\pi/2} < \lambda < \lambda_0$, where $\lambda_{\pi/2}$ and λ_0 are the critical points given by

$$\lambda_{\pi/2} = -(\omega - \nu + \sigma'), \\ \lambda_0 = -\nu [1 + 2(\varepsilon' + \sigma') / (\omega - \varepsilon')]. \quad (28)$$

It is easy to see from the quadratic form (18) that $g < 0$ when $\lambda_- < \lambda < \lambda_+$, where

$$\lambda_\pm = -(\omega - \nu + \sigma') \pm \sqrt{\Delta}, \\ \Delta = (\omega + \sigma')(\omega - 2\nu + \sigma'), \quad (29)$$

are the roots of $g = 0$. Comparing the two ranges in Eqs. (28) and (29), we see that the latter brackets the former, hence the condition $g < 0$ is automatically satisfied once the bent solution exists. Substituting Eq. (28) in (17), we find for the mean fields and their corresponding energy at the critical points

$$\cos \theta|_{\lambda_0} = 1, \quad a_\theta|_{\lambda_0} = a_0, \quad E_\theta|_{\lambda_0} = E_0, \\ \cos \theta|_{\lambda_{\pi/2}} = 0, \quad a_\theta|_{\lambda_{\pi/2}} = 2, \\ E_\theta|_{\lambda_{\pi/2}} = -(\omega - \nu - \varepsilon'). \quad (30)$$

We demonstrate the shape-phase diagram in a simple case with $\varepsilon' = \sigma' = 0$, and $\omega = 3\nu$ in Fig. 1. For $\lambda > \lambda_0 = -\nu$ there is no bent solution and E_0 is the absolute minimum. For $\lambda < \lambda_0$, E_0 becomes a saddle point and E_θ , the absolute minimum. With de-

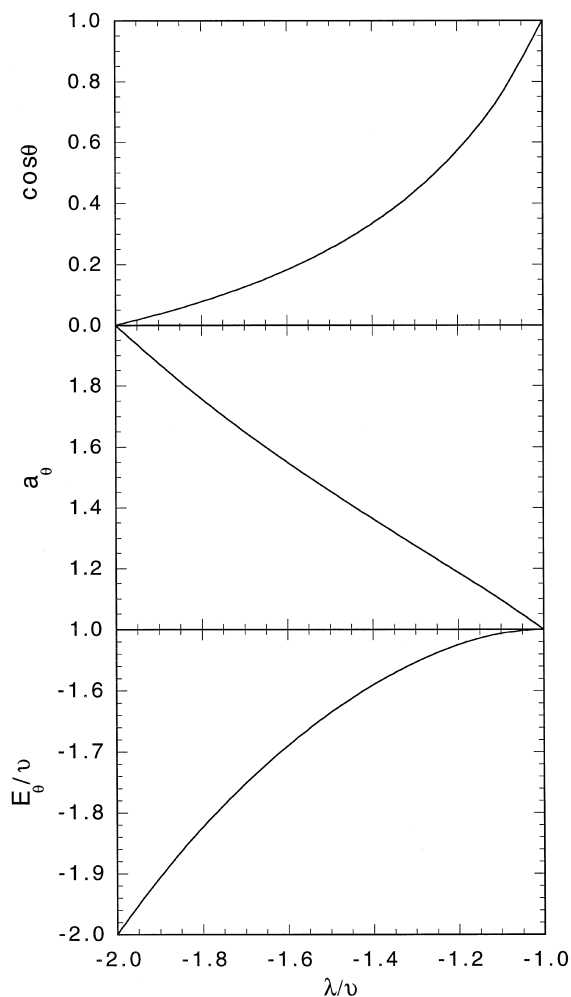


Fig. 1. Shape-phase diagram for XY_2 molecules for the case $\varepsilon' = \sigma' = 0$, and $\omega = 3v$. The mean fields $\cos \theta$, a_0 , and the corresponding energy E_θ are plotted against λ (in units of v).

creasing λ , the bending angle θ increases from 0° until it reaches the maximum value of 90° at $\lambda = \lambda_{\pi/2} = -2v$. At this point $a = 2$ ($r = \infty$), and the molecule is dissociated. Including the ε' and σ' terms in the energy surface shifts the critical points and the values of E_0 and a_0 at λ_0 , but otherwise the main features of the shape-phase diagram in Fig. 1 are maintained.

Interestingly, a shape-phase transition is also possible in the case of a minimal $O_{12}(4)$ dynamical symmetry, i.e., when $\varepsilon' = \sigma' = \lambda_3 = 0$. In this case, λ_4 drives the shape transition and a phase diagram

similar to Fig. 1 is obtained when λ_4 is within the critical points, $-2\kappa_{12} < \lambda_4 < -\kappa_{12}$. Note that the energy of the bending mode in the linear phase is given exactly by $2N(\kappa_{12} + \lambda_4)$, which vanishes at the critical point as it should. In realistic applications [16], λ_4 is determined from the difference of the symmetric and antisymmetric stretching energies, and typically it is positive and smaller than κ_{12} . Therefore, a realistic description of bent XY_2 molecules within the $O_{12}(4)$ dynamical symmetry does not appear to be feasible.

Inclusion of the $U(3)$ terms (specifically λ_3) avoids this problem, in that one can fix λ_4 from the energy difference and use λ_3 to drive the shape transition. The λ_3 term has a small effect on the stretching energies but it has a relatively large contribution to the bending energy. In the linear phase, the bending energy is given by $2N(\kappa_{12} + \lambda_4 + \lambda_3/2) = N(v + \lambda)$ to leading order in N . Thus, the bending energy again vanishes at the critical point $\lambda_0 = -v$.

The above study indicates that shapes in triatomic molecules are mainly determined by the dipole and Majorana interactions, while the other terms based on the \hat{n}_p operator play a small, perturbative role. Thus, to get the main features of shape-phase transitions in XYZ molecules, one can set $\varepsilon'_i = \sigma'_i = \sigma_{12} = 0$ in the energy surface (8). Then one sees from Eqs. (12) and (13) that the solutions for $\theta = 0$ and π are trivially given by $a_1 = a_2 = 1$ with the corresponding energies

$$\begin{aligned} E_0 &= - \left[N_1^2 \kappa_1 + N_2^2 \kappa_2 + N_1 N_2 \kappa_{12} \right], \\ E_\pi &= - \left[N_1^2 \kappa_1 + N_2^2 \kappa_2 - N_1 N_2 (\kappa_{12} + \lambda_4) \right]. \end{aligned} \quad (31)$$

The mean field expressions for the bent solution are slightly more complicated

$$\begin{aligned} a_{1\theta} &= 1 + (v^2 - \lambda^2) \frac{8N_2 \kappa_2 \lambda - N_1 (v^2 + \lambda_3^2 - \lambda_4^2)}{N_1 \left[64\kappa_1 \kappa_2 \lambda^2 - (v^2 + \lambda_3^2 - \lambda_4^2)^2 \right]}, \\ a_{2\theta} &= 1 + (v^2 - \lambda^2) \frac{8N_1 \kappa_1 \lambda - N_2 (v^2 + \lambda_3^2 - \lambda_4^2)}{N_2 \left[64\kappa_1 \kappa_2 \lambda^2 - (v^2 + \lambda_3^2 - \lambda_4^2)^2 \right]}, \\ \cos \theta &= - \frac{v}{\lambda} \left[\frac{(2 - a_{1\theta})(2 - a_{2\theta})}{a_{1\theta} a_{2\theta}} \right]^{1/2}, \end{aligned} \quad (32)$$

with the bent energy given by

$$E_{\theta} = -N_1^2 \kappa_1 a_{1\theta} (2 - a_{1\theta}) - N_2^2 \kappa_2 a_{2\theta} (2 - a_{2\theta}) + \frac{N_1 N_2}{4} \left[\frac{v^2}{\lambda} (2 - a_{1\theta})(2 - a_{2\theta}) + (\lambda_3 - \lambda_4) a_{1\theta} a_{2\theta} + 2\lambda_4 (a_{1\theta} + a_{2\theta}) \right]. \quad (33)$$

An analysis of the three extremum points similar to the XY_2 case above shows that the critical point for the linear to bent shape transition is still given by $\lambda_0 = -v$, and a shape-phase diagram similar to Fig. 1 follows.

In conclusion, we have obtained analytical solutions in a mean field study of triatomic molecules in the vibron model, which clarified the phase transition from linear to bent shape. The shape of triatomic molecules is determined from the competition between the dipole and Majorana interactions. The $U(3)$ Majorana interaction especially plays a critical role in obtaining a bent molecule, while the other interactions in the Hamiltonian are found to play a marginal role. Details of the mean field analysis of shapes in the general case, as well as applications to bent triatomic molecules, will be presented in a longer article.

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