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Rotational-vibrational relative equilibria and the structure of quantum energy spectrum of the tetrahedral molecule P_4

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Abstract. We find relative equilibria (RE) of the rotating and vibrating tetrahedral molecule P_4 and study the correspondence of these RE's to the extremal quantum states in the vibration-rotation multiplet and to the extrema of the semi-quantum rotational energy surfaces obtained for a number of excited vibrational states. To compute the energy of RE's we normalize the full rotation-vibration Hamiltonian H of P_4 in the approximation of nonresonant modes ν_2^E and $\nu_3^{F_2}$ and find the stationary points of the resulting normal form (known as reduced effective Hamiltonian $H_{\rm eff}$) which is defined on the reduced phase space $CP_2{\times}CP_1{\times}S_2$. Most of these points are fixed points of the symmetry group action on $CP_2{\times}CP_1{\times}S_2$. To explain our results in more detail we introduce numerical values of the parameters of H, such as the cubic force constants, using an atom-atom harmonic potential with one adjustable parameter. This simple model gives correct qualitative description of the rotational structure of the lowest excited vibrational states ν_2, ν_3 and $\nu_2+\nu_3$ of P_4.

PACS. 33.15.Mt Rotation, vibration, and vibration-rotation constants – 33.20.Vq Vibration-rotation analysis

1 Introduction

Since the early 80-s classical mechanics has been widely used to give a qualitative description of molecular rotation and vibration (see reviews in [1–5]). Dorney and Watson [6] interpreted quasidegenerate groups of rotational energy levels, the so-called *clusters*, in terms of classical rotation around equivalent symmetry axes of the molecule. Later this approach was developed extensively by Harter and co-workers [7,8]. Notably, the classical rotational Hamiltonian function was introduced as a function $E^J(\varphi,\theta)$ on the rotational phase space S_2 and relation

$$\begin{pmatrix}\hat J_x\\ \hat J_y\\ \hat J_z\end{pmatrix}\to|\mathbf{J}|\begin{pmatrix}\sin\theta\cos\varphi\\ \sin\theta\sin\varphi\\ \cos\theta\end{pmatrix},\quad |\mathbf{J}|=\sqrt{J(J+1)},\qquad(1)$$

was used to obtain classical analogues E^J of the effective quantum rotational Hamiltonians $H(\hat J_x,\hat J_y,\hat J_z)$. The function $E^J(\varphi,\theta)$ was called the *rotational energy surface*. It has one natural parameter, the length of the total angular momentum $\mathbf{J}$, which is a strictly conserved quantity. For a meaningful quantum-classical comparison J should be large.

The symmetry of the molecule defines that of $E^J(\varphi,\theta)$ and in particular the number of equivalent minima and maxima of $E^J(\varphi,\theta)$. It was shown in great detail how these latter correspond to regular sequences of rotational energy levels and clusters.

Stationary points of $E^J(\varphi,\theta)$ correspond to stationary axes of rotation or *rotational relative equilibria* (RE). Many such points are fixed points of the symmetry group action on S_2 and are entirely defined by the symmetry of the system. Žhilinskií and Pavlichenkov [9] made further important step by considering bifurcations of stationary points of $E^J(\varphi,\theta)$, *i.e.*, bifurcations of rotational RE, which occur when J changes. Since J is a measure of rotational excitation of the molecule we can expect that the system of stationary points becomes more complicated when J rises.

Classical limit interpretation of quantum vibrational energy level spectrum began with a 1:1 resonance system whose reduced phase space is a 2-sphere [10], also called a *polyad* sphere [11]. This space is the same as for the rotator and the analysis is similar. The reduced vibrational "polyad" Hamiltonian $H_{\rm vib}$ is a function on S_2. At low vibrational excitation (near the limit of linearization when the perturbation of the 1:1 harmonic oscillator is small) stationary points of $H_{\rm vib}$ correspond to vibrational RE or *nonlinear normal modes* [12–15]. Bifurcations of these RE produce other modes, such as the so-called

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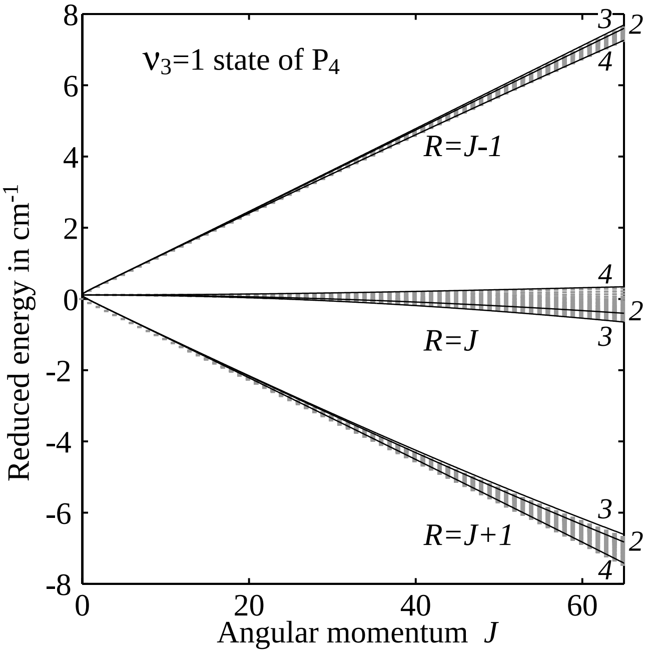

Fig. 1. General view of the three Coriolis branches of the $\nu_3^{F_2} = 1$ fundamental state of P_4 in the experimentally studied range of J values. "Semi-quantum" (lines) and quantum (grey bars) energies are computed using the phenomenological Hamiltonian of Boudon and co-workers in [23] without scalar terms $H_{\mathrm{scalar}}(J)$. Indices 4, 3, and 2 on the right end of semi-quantum lines mark the local symmetries C_4, C_3, and C_2 of stationary points of the rotational energy surfaces.

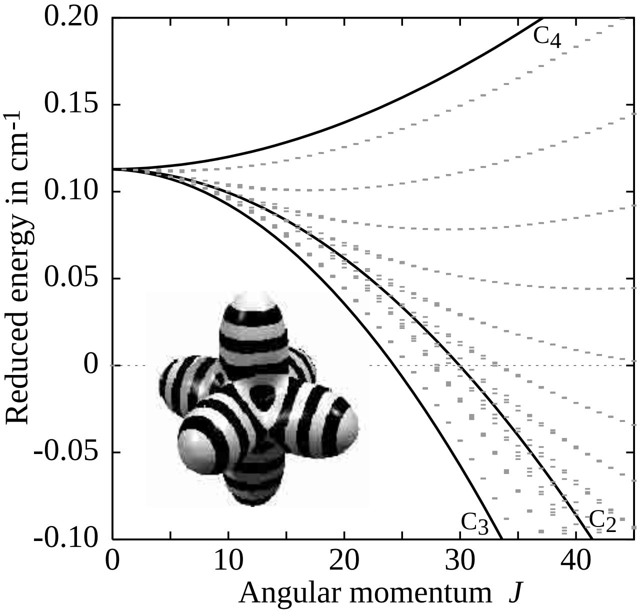

Fig. 2. The central branch F^0 $(J = R)$ of the $\nu_3(F_2) = 1$ state of P_4 computed using the Hamiltonian in reference [23]. Energies of extrema of rotational energy surfaces are shown by lines, horizontal grey bars show quantum energy levels (due to insufficient resolution most clusters of levels are represented by a single bar). Energies are given without the scalar term $H_{\mathrm{scalar}}(J)$, see Section 4.2.

local modes. Generalization to polyads of higher dimensional systems required complex projective (CP) spaces, such as the polyad phase space CP_2 of the 1:1:1 oscillator system [16,17]. Other systems were studied in a similar way [5,11,18].

The first attempt to consider rotational classical limit of excited vibrational states was done in [2,19] where a group of k vibrational states (a polyad) was considered. Each state in the polyad is characterized by its own classical rotational energy function $E_i^J(\varphi, \theta)$ with $i = 1, ..., k$. We call this a "semi-quantum" description, because vibrational degree(s) of freedom are kept quantum. Technically, the functions $E_i^J(\varphi, \theta)$ are eigenvalues of the $k \times k$ matrix of the "semi-quantum" Hamiltonian which is obtained from a quantum rotation-vibration Hamiltonian after replacing all rotational operators according to (1) and is a function of (φ, θ) and vibrational operators. A number of concrete molecular systems was successfully analyzed in this way in [20,21], and most recently in [22].

1.1 Example of semi-quantum description

To get an idea of the kind of understanding of the structure of quantum rotation-vibration energy levels which is obtained in the semi-quantum approach, compare energy levels of the $\nu_3 = 1$ fundamental state of the P_4 molecule and semi-quantum energies of stationary axes of rotation shown in Figures 1 and 2. P_4 is a relatively heavy molecule with a small rotational constant B. The structure of the $\nu_3 = 1$ state of P_4 with its three well-known Coriolis branches (Fig. 1) is typical for tetrahedral and octahedral molecules [24]. The ν_3 vibration induces angular momentum $\boldsymbol{\pi}$ whose amplitude equals 1 in the $\nu_3 = 1$ state. The Coriolis coupling term $B\zeta\,(\boldsymbol{\pi} \cdot \mathbf{j})$ is dominant and the amplitude of $\mathcal{R} = \mathbf{j} - \boldsymbol{\pi}$ (called "rotational" angular momentum) is an approximate constant of motion. The quantum number R equals $J-1$, J, and $J+1$ for the three branches F^-, F^0, and F^+ respectively; each branch has $2R+1$ levels.

In the semi-quantum approach each branch of ν_3 is described by its own rotational energy function $E^J(\theta, \varphi)$. The symmetry group T_d and time reversal symmetry $\mathcal{T}$ combine in such a way that the functions $E^J(\theta, \varphi)$ in the space with coordinates (J_x, J_y, J_z) or (J, θ, φ) have octahedral symmetry. Symmetry axes C_3, C_4, and C_2 are stationary axes of rotation and each function $E^J(\theta, \varphi)$ has 8, 6, and 12 corresponding stationary points. (The number of equivalent symmetry elements C_3, S_4, and C_s in the T_d group is 4, 3, and 6 respectively; each element corresponds to two fixed points on the phase space S_2 which in turn correspond to two different directions of classical rotation.) For example, the rotational energy function for the central branch F^0 is shown in Figure 2. It has maxima at the C_4 points, minima at the C_3 points, and saddle points at C_2. Regular sequences of quantum states can be seen near maximum and minimum semi-quantum energies. In fact these states are highly degenerate 6-fold and 8-fold *clusters* of levels. The C_2 point marks the barrier between the two level systems.

It follows that we can give a comprehensive qualitative description of the underlying quantum energy spectrum on the basis of the semi-quantum description, *i.e.*, knowing the energies of rotation-vibration relative equilibria (RE). Thus we can predict different possible localizations (C_4 and C_3) and estimate the spacing and the number of clusters near the energy of each stable RE using the local one-dimensional oscillator approximation on S_2. Without this kind of simple description, data on quantum energies of individual states and complicated phenomenological model Hamiltonians which reproduce them remain often unsatisfactorily difficult to understand.

1.2 Fully classical description

Given all the development summarized above, an analysis of the quantum rotation-vibration energy spectrum using an *entirely* classical system, *i.e.*, a system for which rotation and vibration are considered classically, appears as the most direct and logical continuation of the previous work. Yet it has not been attempted till very recently in [22] where an application of such analysis for a triply degenerate F_2 state of the tetrahedral molecule $\mathrm{Mo(CO)_6}$ was reported. The authors of [22] based their study on an effective rovibrational Hamiltonian whose terms $(q,p)^2J^k$ had vibrational and rotational part of degree 2 and $k = 0, ..., 3$ respectively. They found that the energies of rotation-vibration RE obtained for the classical analogue of this Hamiltonian and the semi-quantum energies for stationary points of each of the three rotational energy surfaces *matched exactly.* This suggested that even at the lowest vibrational excitation when the system is very far from the vibrational classical limit, classical rotation-vibration relative equilibria remain a useful tool of the analysis of the quantum spectrum. Substantial progress in the comparison of quantum, semi-quantum, and classical description was made at the same time in [26]. This study continued the analysis of a simple one parameter system of two coupled angular momenta $\mathbf{S}$ and $\mathbf{N}$ started in [25]. In our context, such a model can represent polyads of a doubly-degenerated vibrational mode and rotational multiplets. In this article we provide the first detailed report on the entirely classical analysis of the rotation-vibration energy level spectrum of the quantum vibration-rotation Hamiltonian of a concrete system, the tetrahedral molecule P_4. The necessary theoretical background is given in a separate paper [27]; further useful information can be found in the recent review [28].

1.3 Relative equilibria in the ground vibrational state

The phenomenological Hamiltonian H_{eff} (with parameters fitted to experimental data) can only provide information on the energies and stabilities of different RE of the molecule in a particular state. In order to explain and to predict these characteristics our analysis should begin with the initial Hamiltonian H. Even when the potential in H is known poorly, correct qualitative answers and predictions can still be obtained on the basis of very simple models. Thus, using a simple harmonic atom-atom potential we explained in [29] why in the ground vibrational state of P_4 (and of any tetrahedral molecule A_4) the energy of the C_3 relative equilibrium is higher than that of the C_4 equilibrium. Similarly it can be demonstrated that for the ground state of an octahedral molecule B_6 the inverse is true.

We remind that in [29] all vibrations were "frozen", *i.e.*, vibrational kinetic energy was set to zero ($p = 0$) and the Hamiltonian H depended only on rotational variables (j_x, j_y, j_z) and normal mode coordinates q. In this situation, increasing rotational energy causes such distortion of the static equilibrium configuration of the molecule which keeps the total energy H at minimum. Rotational energy is proportional to the amplitude J of the total angular momentum $\mathbf{j}$ and distortion is described by q. If the molecule possesses a rotational RE which corresponds to a stationary axis of rotation with fixed relative values of (j_x, j_y, j_z), we can easily find the energy of such RE by determining the values of $q(J)$ which minimize $H(q; J)$ for each J.

Our present paper extends the above method to excited vibrational states. In this case, vibrational kinetic energy cannot be ignored. Instead, approximate vibrational integrals of motion, the so-called polyad integrals should be introduced and the system should be normalized. This approximation is valid near the limit of linearization (at small vibrational excitations) where we look for relative equilibria. At given fixed values of polyad integral(s) N our normalized Hamiltonian is nothing else but the classical analogue of the effective Hamiltonian H_{eff} used by spectroscopists to study individual quantum states. To characterize relative equilibria (for all J *and* N) we look for stationary points of the normalized Hamiltonian.

1.4 Example: relative equilibria of a diatomic molecule

The essence of our approach can be well illustrated on the example of a diatomic molecule which has already been exploited in [30]. Rotation-vibration of this molecule is described by a reduced two-body Hamiltonian

$$H = \frac{p_r^2}{2\mu} + \frac{j^2}{2\mu r^2} + V(r), \tag{2a}$$

where r and p_r are internuclear coordinate and corresponding conjugated momentum, μ is reduced mass, and $V(r)$ is vibrational potential which can be approximated by a Morse formula

$$V(r) = D_e \left[1 - \mathrm{e}^{-\beta(r-r_e)}\right]^2, \tag{2b}$$

with D_e the dissociation energy, r_e equilibrium internuclear distance, and β a parameter. In the case of nitrogen with $r_e = 1.094 \times 10^{-8}$ cm, $D_e \approx 60\,642$ cm^{-1}, and

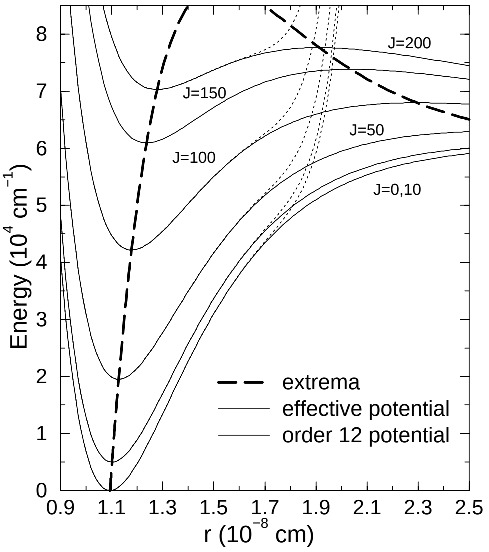

Fig. 3. Effective vibrational potential $V_j(r)$ of the diatomic molecule N_2. Dashed bold lines show the two rotational relative equilibria, dotted lines show an approximation to the potential by a power series in $(r - r_e)$ truncated at degree 12.

$\beta \approx 3.0878 \times 10^8$ cm^{-1}, we obtain the potential $V(r)$ shown in Figure 3.

The amplitude j of the total angular momentum is a constant of motion whose value J can be used as a dynamical parameter. For each J the two last terms in (2a) represent an effective potential $V_j(r)$ (see Fig. 3). The two equilibria of $V_j(r)$ correspond to two rotational relative equilibria of the molecule in the limit of vanishing vibrational kinetic energy, *i.e.*, when $p_r \approx 0$. This is the approximation of [29,30] where such rotational RE are found as solutions to the "static" equations for the extrema of $V_j(r)$.

1.4.1 Vibration-rotation relative equilibria

Our purpose is to show how vibrations should be taken into account in order to find rotation-vibration RE of the molecule. The idea in its simplest form is to *average* rotation-vibration interaction over vibrations. More precisely, in order to account correctly for the kinetic energy term in (2a) we should *normalize* this Hamiltonian near its stable equilibrium at $q = r - r_e = 0$. Assuming that the displacement q is small, we Taylor expand (2a)

$$H = \frac{p_r^2}{2\,m} + \frac{j^2}{2\,mr_e^2} - \frac{j^2 q}{mr_e^3} + \left(\frac{3\,j^2}{2\,mr_e^4} + D_e\,\beta^2\right) q^2 + \ldots$$

This defines a dimensionless smallness parameter

$$\epsilon = r_e^{-1}(2mD_e\beta^2)^{-1/4} = \left(\frac{2B}{\omega}\right)^{1/2}.$$

We Rewrite the series in the form

$$H = \omega\big(H_0 + \epsilon H_1 + \epsilon^2 H_2 + \ldots\big), \qquad (3)$$

with most of the parameters absorbed in ϵ, and then rescale canonical variables q and p_r in order to bring the harmonic part H_0 to the standard form

$$H_0 = \frac{1}{2}(p^2 + q^2),$$

while higher order terms become

$$\begin{aligned}
H_1 &= -\frac{1}{2}\beta r_e\, q^3, \\
H_2 &= \frac{7}{24}(\beta r_e)^2 q^4 + \frac{1}{2} j^2, \\
H_3 &= -\frac{1}{8}(\beta r_e)^3 q^5 - j^2 q, \\
H_4 &= +\frac{31}{720}(\beta r_e)^4 q^6 + \frac{3}{2} j^2 q^2.
\end{aligned}$$

The first order term H_1 equals the Hamiltonian (3) averaged over one period of the orbit of the flow generated by the Hamiltonian vector field X_{H_0}. In order to normalize to higher orders we use the standard Lie series computation [31]. The latter becomes a straightforward oscillator reduction once we introduce an auxiliary 2-oscillator and replace j by

$$j = \frac{1}{4}(p_1^2 + q_1^2 + p_2^2 + p_3^2),$$

so that the above terms H_k become homogeneous polynomials in $(q, p, q_1, p_1, q_2, p_2)$ of degree $k + 2$. The resulting normal form is a Birkhoff series in j and the action integral

$$n = \frac{1}{2}(p^2 + q^2) = H_0.$$

Only even order terms remain in this series,

$$\mathcal{H}_{\rm nf} = \omega\big(H_0 + \epsilon^2 \mathcal{H}_2 + \epsilon^4 \mathcal{H}_4 + \ldots\big),$$

and in particular

$$\begin{aligned}
\mathcal{H}_2 &= \frac{1}{2}\big(j^2 - (\beta r_e)^2 n^2\big), \\
\mathcal{H}_4 &= \frac{3}{2}(1 - \beta r_e) n j^2, \\
\mathcal{H}_6 &= \left(\frac{15}{4} - \frac{15}{2}\beta r_e + \frac{69}{16}(\beta r_e)^2 - \frac{7}{8}(\beta r_e)^3\right) n^2 j^2 - \frac{j^4}{2}.
\end{aligned}$$

With $n = 0$ the above normal form $\mathcal{H}_{\rm nf}$ gives the j-series for the energy of the stable RE of the kind discussed at length in [29,30]; with $j = 0$ the same $\mathcal{H}_{\rm nf}$ gives the Birkhoff n-series for the energy of the nonlinear oscillator with Morse potential $V(r)$; when both n and j are nonzero we obtain vibration-rotation energy.

1.4.2 Quantization

We can now quantize integrals n and j using the well-known rules

$$n = N + \frac{1}{2}, \quad j = \sqrt{J(J+1)},$$

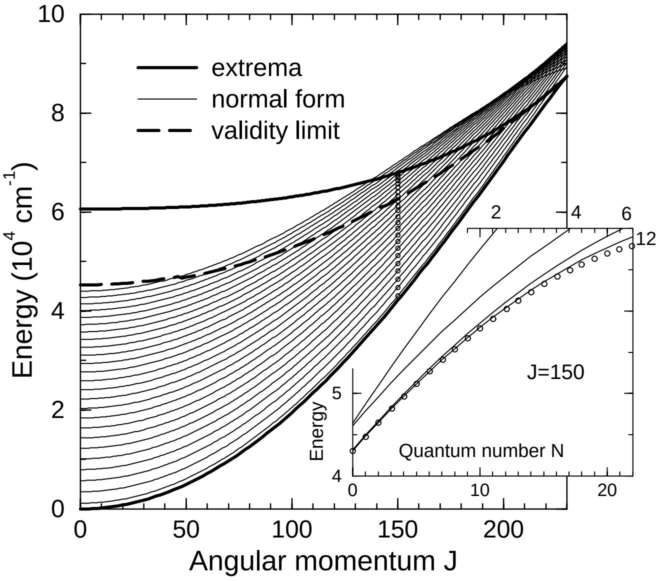

Fig. 4. Quantized energy $\mathcal{H}_{\rm nf}(n,j)$ of the stable RE of the diatomic molecule N_2 (thin lines), and energy of two purely rotational RE (bold lines) as function of J for different fixed $N = n - \frac{1}{2} = 0, 1, ..., 25$. Dashed line gives the upper limit for energies at which the effective potential $V_j(r)$ is correctly represented by a Taylor series truncated to order 12 (see Fig. 3). Circles show exact (WKB) energies for $J = 150$ where the last bound state has $N_{\rm max} = 22$. The insert on the right shows how orders 2, 4, 6, and 12 of the normal form approximate these exact energies. Note that the error of the order 12 normal form $\mathcal{H}_{\rm nf}$ for $n \approx 20$ is larger than the distance in energy between the neighboring quantum states.

where N and J are quantum numbers taking integer values $0, 1, 2, ...$, and compare with exact energies of quantum levels which can be computed using the usual WKB quantization for the action integral

$$S_{h(N),j} = \frac{1}{2\pi}\oint p\,\mathrm{d}q = N + \frac{1}{2}$$

along the orbits of the periodic flow of the vector field X_H of the Hamiltonian (2a) at fixed value of angular momentum j and energy $h(N)$. Results of such computations for the N_2 molecule are presented in Figure 4. It can be seen that within the validity limits of the Taylor expansion of the effective potential function $V_j(q)$ the quantized normal form $\mathcal{H}_{\rm nf}$ describes all vibration-rotation energy levels of the molecule by a unique analytic function $E(N, J)$. In spectroscopy such a function is called a *molecular term* [32] and is traditionally written as

$$\begin{aligned} E_{N,J} = \omega_e\,(N+\tfrac{1}{2}) - \omega_e x_e\,(N+\tfrac{1}{2})^2 + B_e\,J(J+1) \\ - \alpha_e\,(N+\tfrac{1}{2})\,J(J+1) - D_e\,J^2(J+1)^2 + ... \end{aligned}$$

Comparing to $\mathcal{H}_{\rm nf}$ we find spectroscopic parameters of $E_{N,J}$ for the particular potential (2b)

$$B_e = \frac{\omega}{2}\epsilon^2 = \frac{1}{2m\,r_e^2}, \qquad \alpha_e = \frac{3}{2}\omega(\beta r_e - 1)\epsilon^4,$$

$$D_e = \frac{\omega}{2}\epsilon^6, \qquad \text{and} \quad x_e = \frac{1}{2}(\beta r_e)^2\epsilon^2.$$

1.4.3 Generalization to polyatomic molecules

To conclude our example we remark that the diatomic molecule system has only one vibrational degree of freedom and our system is integrable. In the bounded motion domain the integral n is the total action integral and the classical energy E is a real analytic function of n and j which represents the energy of stable rotation-vibration RE of the diatomic molecule.

For a polyatomic molecule the situation is quite different. The system is not integrable and the quantity n can only be introduced as an approximate integral of motion when the system is normalized. This approximate integral represents the dynamical symmetry of the zero order system (harmonic oscillator H_0) and can be associated intuitively with the "size" of the area in the phase space occupied by the trajectories of the vibrating polyatomic molecule (at given energy). We used the same approach for a diatomic molecule and compared the results to an exact solution in order to give a detailed illustration of the main technique of our work.

1.5 Summary of the paper

In this paper we study vibration-rotation relative equilibria of the four-atomic molecule P_4 using the approach presented in the previous section. We begin with the full vibration-rotation Hamiltonian and introduce a potential which is both simple and sufficiently realistic. Then we introduce approximate dynamical vibrational symmetry and corresponding integral(s) n and normalize this initial Hamiltonian accordingly. The normal form $\mathcal{H}_{\rm nf}$ defines equations of motion of the reduced system at fixed n and j whose values are parameters. Relative equilibria are stationary solutions of these equations. The number of different RE at each value of (n, j) is greater or equal the number of degrees of freedom of the reduced system. Consequently, contrary to the case of a diatomic molecule, at each value of (n, j) we have a range of energies accessible to the system. In quantum mechanics we have the corresponding multiplet or polyad of quantum states, such as shown in Figures 1 and 2.

The P_4 molecule has six vibrational degrees of freedom which constitute the nondegenerate "breathing" mode A_1, and the doubly and triply degenerate modes E and F_2. We use the simplified notation for the coordinates and conjugated momenta of these modes given in Table 1 and we also use complex oscillator variables

$$z = q + \mathrm{i}p, \quad \bar{z} = q - \mathrm{i}p. \tag{4}$$

Table 1. Notation for vibrational and rotational dynamical variables of P_4.

subsystem	traditional notation	this paper
F_2 mode	$q_\alpha^{F_2}$, $p_\alpha^{F_2}$, $\alpha = x, y, z$	q_i, p_i, $i = 1, 2, 3$
E mode	q_α^E, p_α^E, $\alpha = a, b$ or $1, 2$	q_i, p_i, $i = 4, 5$
A_1 mode	q^{A_1}, p^{A_1}	q_a, p_a
rotation[a]	momenta j_α, $\alpha = x, y, z$	q_i, p_i, $i = 6, 7$

[a] instead of the angular momentum components j_α we use four dynamical variables describing the 1:1 oscillator, see Section 2.3.

The zero order vibrational Hamiltonian H_0 of P_4 represents a 1-oscillator, a 1:1 oscillator, and a 1:1:1 oscillator with frequencies ω_{A_1}, ω_E and ω_{F_2} respectively. We assume the absence of any resonances, *i.e.*, we suppose that these frequencies are incommensurate. Then three approximate integrals of motion, the polyad integrals n_a, n_e, and n_f with values N_a, N_e, and N_f respectively, can be introduced and perturbations of each of the oscillators can be reduced so that in particular all crossed (interaction) terms, such as $q^E q^{F_2}$ or $q^{A_1} q^E q^{F_2}$ etc., are eliminated from the normal form H_{eff}. The remaining terms can be expressed as various powers of dynamical invariants [27]. In particular, all dependence of H_{eff} on the A_1 mode variables is expressed as power series in n_a. This happens because the A_1 vibration does not change the geometry of the molecule. So, for simplicity, we will ignore this mode (in other words we will assume that $n_a = N_a = 0$).

Reduction in the absence of resonances between different vibrational modes introduces reduced phase spaces for each of the subsystems; the F_2 and E mode reduced phase space is a complex projective space CP_2 and CP_1 respectively (recall that CP_1 and S_2 are diffeomorphic), and the reduced phase space for the A_1 mode is just a point. The reduced phase space of the rotational subsystem with conserved total angular momentum j is S_2. Neglecting the A_1 mode, the total reduced phase space is the direct product $CP_2 \times CP_1 \times S_2$.

To find relative equilibria (RE) we look for such stationary points of the normal form H_{eff} on $CP_2 \times CP_1 \times S_2$ which exist anywhere close to the limit of linearization (*i.e.*, at any small perturbation ϵ). Most of the RE are entirely defined by the symmetry of our system. These RE correspond to the stationary points of H_{eff} which lie on the critical orbits of the symmetry group action on $CP_2 \times CP_1 \times S_2$ (they are isolated fixed points of the group action). To find these points we should analyze the group action.

The discrete symmetry group of our system is an extension of the spatial symmetry group T_d of the equilibrium configuration of P_4 by the time reversal operation (also called momentum reversal) which acts on the dynamical variables as follows

$$(j_1, j_2, j_3) \to (-j_1, -j_2, -j_3), \tag{5a}$$

$$(z_1, ..., z_5) \to (\bar{z}_1, ..., \bar{z}_5). \tag{5b}$$

The extended group can be represented as a direct product $T_d \times Z_2$ of T_d and an abstract group of order 2 and is isomorphic to the O_h group [27]. Like in [27], we use the notation $\mathcal{T}$ instead of plain Z_2 to underline association of this group with time reversal. The group action of $T_d \times \mathcal{T}$ on $CP_2 \times CP_1 \times S_2$ and on its different subspaces is studied in [27] where coordinates of all critical orbits and invariant subspaces of this action are given.

An elementary study of the stability of relative equilibria is important for the comparison to quantum mechanics. Near a sufficiently stable RE we can expect to find localized quantum states. The energy of such states can be estimated using a local approximation for small oscillations about the RE. The number of equivalent RE defines the number of quasi-degenerated localized states (a *cluster*). Many examples can be found in the rotational system and in vibrational systems with two degrees of freedom. In the latter case, the nodes of localized wavefunctions lie along the RE and the number of nodes gives the polyad number [15]. Stability of RE is also required when Morse conditions for the stationary points of the reduced Hamiltonian H_{eff} are checked in order to determine whether all RE are found.

The rest of this paper is organized as follows. In Section 2 we define the complete rotation-vibration Hamiltonian for the four-atom tetrahedral molecule P_4; we also introduce a simple model potential of P_4 with one phenomenological force constant K. In Section 3 we reduce this Hamiltonian in the approximation of polyads formed by nonresonant modes ν_2^E and $\nu_3^{F_2}$, *i.e.*, assuming incomparable frequencies of the E and F_2 modes and neglecting the totally symmetric "breathing" mode A_1. This step is similar to quantum reduction (known as contact transformation) which is widely used in spectroscopy [33]. We express our reduced Hamiltonian H_{eff} (the normal form) in terms of a symmetry adopted rovibrational polynomial basis similar to the one used by spectroscopists. In Section 4 we study relative equilibria as stationary points of H_{eff} on $CP_2 \times CP_1 \times S_2$. We introduce the integrals of motion N_e, N_f, and J and the reduced phase space $CP_2 \times CP_1 \times S_2$. Using coordinates of critical orbits of the action of the finite symmetry group on $CP_2 \times CP_1 \times S_2$ found in [27] we obtain the value of H_{eff} on the critical orbits. This gives analytic expression for the energy of RE's as function of N_e, N_f, and J. We also find additional RE which correspond to non-critical orbits. In Section 5 we determine the values of the two parameters, the atom-atom harmonic potential constant K and the equilibrium distance P–P, which enter in our formulae together with N_e, N_f, and J. To this end we use the comparison to the phenomenological spectroscopic study of the $\nu_3^{F_2}$ fundamental ($N_e = 0, N_f = 1$) by Boudon and co-workers [23]. We follow by computing predictions for the E-state ($N_f = 0, N_e = 1$), the combination state ($N_f = 1, N_e = 1$), and some higher polyads.

2 Full rotation-vibration Hamiltonian of P_4

Our derivation of the rotation-vibration Hamiltonian H follows the classic spectroscopic procedure in Chapter 11 of [34], see also [35,36]. After excluding translation of the center of mass, we assume that the atoms of P_4 vibrate about a well defined static equilibrium configuration and that the amplitudes of vibrations are small, so that the frame rotating with the molecule is also meaningfully defined.

2.1 Kinetic energy

To find the kinetic energy we begin with the velocity of each atom $i = 1, ..., 4$ in the rotating frame

$$\Omega \wedge \left(\mathbf{R}_i^0 + \mathbf{r}_i\right) + \dot{\mathbf{r}}_i, \tag{6a}$$

where Ω is the vector of angular velocity, and $\mathbf{R}_i^0$ and $\mathbf{r}_i$ give equilibrium position and displacement of atom i respectively. All *allowed* displacements are defined by normal modes

$$\mathbf{r}_i = \sum q_k \boldsymbol{\varrho}_k^i, \quad k = A_1, E_a, E_b, F_{2x}, F_{2y}, F_{2z}, \tag{6b}$$

and obey automatically the center of mass and the Eckart condition

$$\sum_i m_i \mathbf{u}_i = 0, \quad \mathbf{u}_i = \mathbf{r}_i, \dot{\mathbf{r}}_i, \, (\mathbf{R}_i^0 \wedge \mathbf{r}_i), \, (\mathbf{R}_i^0 \wedge \dot{\mathbf{r}}_i). \tag{6c}$$

The kinetic energy T can be now written as

$$2T = \sum_i m_i \left[(\Omega \wedge (\mathbf{R}_i^0 + \mathbf{r}_i))^2 + \dot{\mathbf{r}}_i^2 + 2\Omega(\mathbf{r}_i \wedge \dot{\mathbf{r}}_i) \right], \tag{7}$$

where the displacement and internal velocity of each atom are functions of six normal mode coordinates and corresponding time derivatives, *i.e.*, $\mathbf{r}_i = \mathbf{r}_i(q)$ and $\dot{\mathbf{r}}_i = \dot{\mathbf{r}}_i(\dot{q})$. To rewrite T in the Hamiltonian form we define the generalized momenta

$$j_\alpha = \frac{\partial T}{\partial \Omega_i}, \; \alpha = x, y, z, \quad p_k = \frac{\partial T}{\partial \dot{q}_k}, \tag{8}$$

so that the kinetic energy in (7) becomes

$$2T = (\mathbf{j} - \boldsymbol{\pi})^T \boldsymbol{\mu}(q) \; (\mathbf{j} - \boldsymbol{\pi}) + \sum \frac{p_k^2}{m} \, . \tag{9}$$

This expression plus a vibrational potential $U(q)$ is often called the *Howard-Wilson Hamiltonian* [37].

Direct calculation using normal mode definitions in [29] gives concrete expressions for $\boldsymbol{\pi}$ and $\boldsymbol{\mu}$ in the case of P_4. The 3-vector $\boldsymbol{\pi}$ is the angular momentum induced by the vibration,

$$\begin{aligned}
\pi_1 &= \frac{1}{2}\Big(p_2 q_3 - p_3 q_2 + q_5 p_1 - p_5 q_1 + \sqrt{3}(q_4 p_1 - p_4 q_1)\Big), \\
\pi_2 &= \frac{1}{2}\Big(p_3 q_1 - p_1 q_3 + q_5 p_2 - p_5 q_2 + \sqrt{3}(p_4 q_2 - q_4 p_2)\Big), \\
\pi_3 &= \frac{1}{2}\Big(p_1 q_2 - p_2 q_1\Big) + p_5 q_3 - p_3 q_5 .
\end{aligned}$$

The matrix $\boldsymbol{\mu}$ is the inverse of the matrix of the modified inertia tensor

$$I' = mR^2 \left[1 + \frac{2\sqrt{2}}{\sqrt{3}} q_a + \frac{2}{3} q_a^2 + \mathcal{I}(q) \right], \tag{10}$$

where

$$\begin{aligned}
\mathcal{I}_{1,1} &= -\frac{1}{\sqrt{3}} q_4 + q_5 - \frac{\sqrt{2}}{3} q_a q_4 + \frac{\sqrt{2}}{\sqrt{3}} q_a q_5 \\
&\quad + \frac{1}{12}\big(q_4 - \sqrt{3}\, q_5\big)^2 + \frac{1}{4}\big(q_3^2 + q_2^2\big) \\
\mathcal{I}_{2,2} &= -\frac{1}{3}(q_4 + \sqrt{3}\, q_5)(\sqrt{2} q_a + \sqrt{3}) \\
&\quad + \frac{1}{12}\big(q_4 + \sqrt{3}\, q_5\big)^2 + \frac{1}{4}\Big(q_1^2 + q_3^2\Big) \\
\mathcal{I}_{3,3} &= +\frac{2}{\sqrt{3}} q_4 + \frac{2\sqrt{2}}{3} q_a q_4 + \frac{1}{3} q_4^2 + \frac{1}{4}\Big(q_1^2 + q_2^2\Big), \\
\mathcal{I}_{1,2} &= -q_3 - \frac{\sqrt{2}}{\sqrt{3}} q_a q_3 + \frac{\sqrt{3}}{6} q_4 q_3 + \frac{1}{4} q_1 q_2, \\
\mathcal{I}_{1,3} &= -q_2\Big(1 + \frac{\sqrt{2}}{\sqrt{3}} q_a + \frac{\sqrt{3}}{12} q_4 + \frac{1}{4} q_5\Big) + \frac{1}{4} q_3 q_1, \\
\mathcal{I}_{2,3} &= -q_1\Big(1 + \frac{\sqrt{2}}{\sqrt{3}} q_a + \frac{\sqrt{3}}{12} q_4 - \frac{1}{4} q_5\Big) + \frac{1}{4} q_2 q_3 .
\end{aligned}$$

2.2 Model potential

The potential energy $U(q)$ of P_4 is known poorly. The harmonic atom-atom potential

$$2U(q) = K \sum_{i,j>i}^{4} \Big[|\mathbf{R}_i^0 + \mathbf{r}_i(q) - \mathbf{R}_j^0 - \mathbf{r}_j(q)| - R \Big]^2, \tag{11}$$

provides a simple model which implies that the potential energy of the molecule depends only on the deformation of the six atom-atom bond lengths. This potential was already used in [29] to obtain a qualitatively correct description of the rotational RE of P_4 in the absence of vibrations (when all $p_k = 0$) and we can expect that it will work as well when vibrations are excited ($p_k \neq 0$). There are two unknown parameters in (11), the value of $R = |\mathbf{R}_i^0|$ defining the "size" of the molecule, and the harmonic force constant K of the P–P bond. The former parameter can be determined from the rotational constant B while K can be adjusted in order to reproduce most closely the values of the three harmonic normal mode frequencies ω_{F_2}, ω_E, and ω_{A_1} (see Sect. 5.2.1).

2.3 Series expansion and parameterization

To represent the initial rotation-vibration Hamiltonian H as a power series in dynamical variables in Table 1,

$$\begin{aligned}
H &= H_0 + \epsilon H_1 + \epsilon^2 H_2 + ... \\
&= z^2 + \epsilon z^3 + \epsilon^2 z^4 + ...,
\end{aligned} \tag{12}$$

we Taylor expand $H = T(q,p,j) + U(q)$ in q and rescale (p,q) to bring the harmonic part H_0 to the standard form

$$H_0 = \omega_{A_1} n_a + \omega_E n_e + \omega_{F_2} n_f + 0j \ , \tag{13}$$

where n_a, n_e, n_f, and j are harmonic oscillators,

$$\begin{aligned} n_a &= \frac{1}{2}(p_a^2 + q_a^2) = \frac{1}{2}(z_a \bar{z}_a), \\ j &= \frac{1}{4}(p_6^2 + q_6^2 + p_7^2 + q_7^2) = \frac{1}{4}(z_6\bar{z}_6 + z_7\bar{z}_7), \\ n_e &= \frac{1}{2}(p_4^2 + q_4^2 + p_2^5 + q_5^2) = \frac{1}{2}(z_4\bar{z}_4 + z_5\bar{z}_5), \\ n_f &= \frac{1}{2}\sum_{k=1}^{3}(p_k^2 + q_k^2) = \frac{1}{2}(z_1\bar{z}_1 + z_2\bar{z}_2 + z_3\bar{z}_3). \end{aligned}$$

For the uniformity of the approach and of calculations we represent rotational dynamical variables j_1, j_2, j_3 of the initial Hamiltonian (components of the total angular momentum $\mathbf{j}$) using coordinates and conjugated momenta of an auxiliary 1:1 oscillator with exact S_1 symmetry and corresponding strict integral of motion j defined above. Since j is quadratic in (p,q) the frequency of this auxiliary oscillator formally equals 0 (and the rigid rotor energy Bj^2 is the lowest order purely rotational perturbation of degree 4). We use standard oscillator expressions for the components of $\mathbf{j}$,

$$\begin{pmatrix} j_1 \\ j_2 \\ j_3 \end{pmatrix} = \frac{1}{4}\begin{pmatrix} z_6\bar{z}_6 - z_7\bar{z}_7 \\ z_6\bar{z}_7 + z_7\bar{z}_6 \\ \mathrm{i}(z_6\bar{z}_7 - z_7\bar{z}_6) \end{pmatrix} \tag{14}$$

and use (4) to replace all (q,p)'s for z's. This gives

$$H = \omega(H_0 + \epsilon H_1 + \epsilon^2 H_2 + \epsilon^3 H_3 + ...) \tag{15a}$$

where

$$H_0 = \sqrt{2} n_f + n_e + 2n_a + 0j, \tag{15b}$$

and ω is an "adjustable" parameter,

$$\omega = \sqrt{\frac{K}{m}} = \frac{\omega_{F_2}}{\sqrt{2}} = \omega_E = \frac{1}{2}\omega_{A_1}. \tag{15c}$$

With ω in (15a) factored out, the smallness parameter ϵ absorbs all residual dependence on the force constant K and mass m,

$$\epsilon = \frac{1}{R(Km)^{1/4}} \cdot \tag{15d}$$

Note that H_2 contains the rigid rotor term $\frac{1}{2}j^2$. Since the rigid rotor energy is written as

$$B_e j^2 = \frac{1}{2mR^2} j^2 \tag{15e}$$

it also follows that

$$\epsilon^2 = \frac{2B_e}{\omega} \cdot \tag{15f}$$

Different perturbation terms in (15a) are characterized in Table 2.

Table 2. Rotation-vibration perturbation terms.

order	degree	type of the term
ϵ	z^3	cubic anharmonic terms
ϵ^2	z^4	quartic anharmonic terms
	$z^2 j$	Coriolis interaction
	j^2	"rigid rotor" rotation

3 Normalization and reduction

The approximate dynamical symmetry of the system with Hamiltonian (15a) is defined by the zero-order term H_0 in (15b). We assume that the frequencies of the three modes A_1, E and F_2 are incommensurate. (In our model (11) this holds for ω_{F_2} and ω_E whose ratio equals $\sqrt{2}$.) Then the four vector fields X_{n_a}, X_{n_f}, X_{n_e}, and X_j define an approximate dynamical symmetry group of the 4-torus. Normalization of Hamiltonian (12) removes all terms which do not commute with integrals n_a, n_f, n_e, and j. (Note that *a priori* $\{H, j\} = 0$ since the total angular momentum j is a strict integral.) Remaining terms in the normal form H_{eff} are symmetric with regard to the dynamical group; H_{eff} is an effective rotation-vibration Hamiltonian describing polyads of nonresonant modes A_1, E, and F_2.

3.1 Reduction

In the absence of resonance the two components

$$X_f = \sum_{i=1}^{3}\left[z_i\frac{\partial}{\partial z_i} - \bar{z}_i\frac{\partial}{\partial \bar{z}_i}\right], \quad X_e = \sum_{i=4}^{5}\left[z_i\frac{\partial}{\partial z_i} - \bar{z}_i\frac{\partial}{\partial \bar{z}_i}\right]$$

of the vector field of H can be separated so that the corresponding flows φ_f and φ_e define two distinct dynamical S_1 symmetries. The action of these symmetries on the initial vibrational phase space ($C_3 \times C_2$ with coordinates $z_1, ..., z_5$) is free and proper. In the case of φ_f we map the S_1 orbits

$$\varphi_f\colon\ (t_f, z) \to \exp(\mathrm{i}t_f)z,$$

where $z = (z_1, z_2, z_3)$, and $\frac{1}{2}|z|^2 = n_f = const$, to distinct points in CP_2, *i.e.*, we identify all points z in C_3, the initial phase space of the F_2 mode, which have the same module $\sqrt{n_f/2}$ and differ only in common phase $\exp(it_f)$. Similarly we map the S_1 orbits

$$\varphi_e\colon\ (t_e, z) \to \exp(\mathrm{i}t_e)z, \quad z = (z_4, z_5),$$

to points on the 2-sphere S_2 (or on CP_1). In particular, since points (z_1, z_2, z_3) with $t_f = 0$ and $(-z_1, -z_2, -z_3)$ with $t_f = \pi$ lie on the *same* orbit, inversion in the initial space C_3 reduces to *identity* in CP_2. Therefore, when we analyze the image of the finite symmetry group of our system in the reduced phase space $CP_2 \times S_2$ we should only consider proper rotations of the initial phase space *and* momentum reversal in (5b).

3.2 Coordinates on the reduced phase space

The reduced phase space of our system is a direct product of the F_2-mode space CP_2, the E mode space $CP_1 \sim S_2$, and the rotational sphere S_2 characterized by the values N_f, N_e, and J of polyad integrals n_f, n_e, and of the total angular momentum j respectively [27]. Each relative equilibrium (RE) of our system is an equilibrium of $H_{\rm eff}$ and is represented by a point on this reduced phase space $CP_2 \times CP_1 \times S_2$. Like any other orbits of the action of the dynamical symmetry, relative equilibria can be uniquely characterized by the values of dynamical invariants [27]. However, we can also use initial coordinates $(z, \bar{z})$ or charts.

For example, the E-mode sphere S_2 is defined by the equation

$$v_1^2 + v_2^2 + v_3^2 = \frac{1}{4} n_e^2 = const,$$

where dynamical invariants v_1, v_2, and v_3 are defined similar to j_1, j_2, and j_3 as quadratic polynomials in $(z_4, \bar{z}_4, z_5, \bar{z}_5)$ [27]. Any point on this sphere can be defined by the values of (v_1, v_2, v_3) keeping in mind that $v_1^2 + v_2^2 + v_3^2$ equals a constant $\frac{1}{4} N_e^2$. The same point on the diffeomorphic space CP_1 can be defined using $z = (z_4, z_5)$ if we remember that $|z_4|^2 + |z_5|^2 = 2n_e$ is fixed and ignore the common phase. Similarly, coordinates $(j_1, j_2, j_3) = (0, 1, 0)$, $z = (1, -{\rm i})$, $z = ({\rm i}, 1)$, and $z = ({\rm i}e^{{\rm i}\phi}, e^{{\rm i}\phi})$ define the *same* point on the rotational sphere $S_2 \sim CP_1$. In general, we can define a point on CP_k using $k+1$ complex coordinates $z = (z_1, z_2, ..., z_{k+1})$ on C_{k+1} if $|z_1|^2 + |z_2|^2 + \cdots |z_{k+1}|^2$ is a constant and points z and $z \exp({\rm i}\phi)$ with the common phase $0 \le \phi \le 2\pi$ are considered as the same point.

3.3 Normal form

Once the Hamiltonian H is put in the oscillator form (15a) we can use the standard Lie transform method [31] to normalize H. All odd orders (odd degrees in (z, z^*)) vanish in the resulting normal form which is a power series in ϵ^2,

$$\mathcal{H}_{\rm nf} = \omega (H_0 + \epsilon^2 \mathcal{H}_2 + \epsilon^4 \mathcal{H}_4 + \epsilon^6 \mathcal{H}_6 + ...), \qquad (16)$$

whose terms $\mathcal{H}_{2k}$ Poisson commute with H_0. To obtain the reduced Hamiltonian $H_{\rm eff}$, we express all terms in (16) as functions of basic invariant polynomials [27], *i.e.*, as functions on the reduced phase space $CP_2 \times CP_1 \times S_2$. Due to algebraic dependencies between these polynomials (or "sygyzies") a special polynomial basis, such as a Gröbner basis or an integrity basis [27] should, in general, be constructed. We use the tensorial basis described in Section 3.4 below. At the same time, in order to study the dynamics of the reduced system, *i.e.*, to study equations of motion on $CP_2 \times CP_1 \times S_2$, and in particular to study equilibria of $H_{\rm eff}$, we should know expression of $H_{\rm eff}$ in terms of dynamical variables of the initial or of the reduced system, see [27] for more details.

Table 3. Effective rotation-vibration polyad basis for the tetrahedral molecule A_4 with the full symmetry group $T_d \times \mathcal{T}$ in the limit of non-resonant vibrational modes E and F_2 (denoted e and f). The × sign and brackets denote tensor products with respect to the T_d group; the $\oplus$ subscript indicates explicit $\mathcal{T}$-symmetrization $\frac{1}{2}(V + \bar{V})$. Note that quantum operators a and a^+ correspond to $z/\sqrt{2}$ and $\bar{z}/\sqrt{2}$ respectively.

notation	explicit tensorial definition
$H^0_{\alpha\alpha}$	$\frac{1}{2} \sum_i^{[\alpha]} \bar{z}_{\alpha i} z_{\alpha i}$
$H^{\Omega(K,\Gamma)}_{\alpha\beta}$	$\frac{1}{2} \left[[\bar{z}_\alpha z_\beta]^\Gamma \times R^{\Omega(K,\Gamma)} \right]^{A_1}$
$V^\Gamma_{\alpha\beta\alpha\beta}$	$\frac{1}{4} \left[(\bar{z}_\alpha \bar{z}_\beta)^\Gamma \times (z_\alpha z_\beta)^\Gamma \right]^{A_1}$
$H^{1(1,F_1)}_{(\alpha\beta)\Gamma_1(\alpha\beta)\Gamma_2}$	$\frac{1}{4} \left[\left[(\bar{z}_\alpha \bar{z}_\beta)^{\Gamma_1} \times (z_\alpha z_\beta)^{\Gamma_2} \right]^{F_1} \times R^{1(1,F_1)} \right]^{A_1}$
$V_{\alpha\alpha\Gamma'\beta\Gamma\alpha\alpha\Gamma''\beta\Gamma}$	$\frac{1}{8} \left[\left[(\bar{z}_\alpha \bar{z}_\alpha)^{\Gamma'} \times \bar{z}_\beta \right]^\Gamma \times \left[(z_\alpha z_\alpha)^{\Gamma''} \times z_\beta \right]^\Gamma \right]^{A_1}_\oplus$

3.4 Tensorial basis

Tensorial bases are widely used in spectroscopy to account for specific symmetries and to represent effective Hamiltonians. Polynomials in tensorial bases are constructed according to the tensor product rules of the symmetry group of the effective Hamiltonian. To respect dynamical symmetries the number of z variables of each mode (E and F_2) should equal the number of $\bar{z}$ variables of the same mode. (In quantum mechanics this corresponds to diagonal polyad tensor operators with the same number of creation and annihilation operators for each mode.)

As an example consider a purely vibrational quartic anharmonic term V in $\mathcal{H}_2$. To be dynamically symmetric (*i.e.*, to Poisson commute with H_0) V has to be of the type $\bar{z}\bar{z}zz$. With the mode restrictions also taken into account, there can be only three possibilities

$$\bar{z}_f \bar{z}_f z_f z_f, \quad \bar{z}_f \bar{z}_e z_f z_e, \quad \bar{z}_e \bar{z}_e z_e z_e,$$

where f and e stand for any of the indices $(1, 2, 3)$ and $(4, 5)$ respectively (see Tab. 1). At the same time, V should be totally symmetric with regard to the symmetry group $T_d \times \mathcal{T}$ of the initial Hamiltonian. Such symmetrized quartic products can be constructed as tensor products of two factors which transform according to the same irreducible representation Γ of T_d (see Tab. 3). For example consider

$$V^{F_1}_{efef} = \left[\left(\bar{z}^E \bar{z}^{F_2} \right)^{F_1} \times \left(z^E z^{F_2} \right)^{F_1} \right]^{A_1} = \frac{1}{\sqrt{3}} \sum_{\sigma=1}^{3} \bar{\mathcal{V}}^{F_1}_\sigma \mathcal{V}^{F_1}_\sigma,$$

where $\mathcal{V}^{F_1}_\sigma$ with $\sigma = 1, 2, 3$, is a tensor product

$$\mathcal{V}^{F_1}_\sigma = \left(z^E \times z^{F_2} \right)^{F_1}_\sigma = \sqrt{3} \sum_{\sigma'=1}^{2} \sum_{\sigma''=1}^{3} \begin{pmatrix} E & F_2 & F_1 \\ \sigma' & \sigma'' & \sigma \end{pmatrix} z^E_{\sigma'} z^{F_2}_{\sigma''}$$

and $\bar{\mathcal{V}}_\sigma^{F_1}$ is obtained from $\mathcal{V}_\sigma^{F_1}$ by conjugation $z \rightarrow \bar{z}$. Using Clebsch-Gordon coefficients for the T_d group [38] we find

$$\mathcal{V}^{F_1} = \frac{1}{2} \begin{pmatrix} (z_5 + z_4\sqrt{3})z_1 \\ (z_5 - z_4\sqrt{3})z_2 \\ -\,2\, z_5 z_3 \end{pmatrix}.$$

Rotational tensors are built directly from the components of the total angular momentum (j_1, j_2, j_3). We use tensors $R_\sigma^{\Omega(K,\Gamma)}$ constructed by Moret-Bailly [38,39,46] for the group chain $\mathrm{O}(3) \supset O_h$. Here Ω is the total degree in (j_1, j_2, j_3), $K \leq \Omega$ is the index of the irreducible representation of the O(3) group, and (Γ, σ) is the irreducible representation of O_h and its row (projection). Odd-K rotational tensors are antisymmetric with regard to time reversal in (5a). As a consequence, vibrational part of rotation-vibration tensors with odd K should be antisymmetric with regard to (5b). For example, the F_2 mode Coriolis term has the form

$$H_{ff}^{1(1,F_1)} = \frac{1}{4\sqrt{3}} \sum_{\sigma=1}^{3} \left[z^{F_2} \times \bar{z}^{F_2} \right]_\sigma^{F_1} R_\sigma^{1(1,F_1)}.$$

Both the vibrational part of this tensor

$$\left[z^{F_2} \times \bar{z}^{F_2} \right]^{F_1} = \frac{1}{\sqrt{2}} \begin{pmatrix} z_3\bar{z}_2 - z_2\bar{z}_3 \\ z_1\bar{z}_3 - z_3\bar{z}_1 \\ z_2\bar{z}_1 - z_1\bar{z}_2 \end{pmatrix}$$

and the rotational part

$$R^{1(1,F_1)} = 2\mathrm{i}(j_1, j_2, j_3)$$

are antisymmetric with regard to time reversal $\mathcal{T}$.

All different types of tensor constructions required to express the normal form (16) up to order $\mathcal{H}_4$ are summarized in Table 3. Our definitions follow plain tensor product notation albeit for a few commonly used polynomials, such as harmonic terms $n_e = H_{ee}$, $n_f = H_{ff}$, and j^2. We also introduce an additional factor $2^{-k/2}$, where k is the degree in vibrational variables $(z, \bar{z})$, to account for the difference between the classical dynamic variables and quantum creation-annihilation operators

$$a = \frac{1}{\sqrt{2}}(q - \mathrm{i}p), \quad a^+ = \frac{1}{\sqrt{2}}(q + \mathrm{i}p).$$

We should note that our tensorial construction produces complete sets of polynomials of any given degree in $(z, \bar{z})$ but, contrary to an integrity basis or a Gröbner basis, *does not* guarantee linear independence. Up to order six we did not encounter this difficulty, but it can become a problem for larger degrees.

3.5 Parameters of the reduced Hamiltonian

Expression of the normal form (16) in terms of the symmetry-adopted tensorial basis (Tab. 3) is presented in Tables 4 and 5. Comparison of these results to spectroscopic parameters is straightforward. The values of the latter equal the coefficients in Table 4 times $\omega\epsilon^k$ where k is the order of the term. The values of ω and ϵ themselves should be determined from a spectroscopic or *ab initio* study as we do in Section 5.2.1.

Table 4. Effective rovibrational polyad Hamiltonian (normal form) of the P_4 molecule calculated with a harmonic atom-atom potential in the limit of non-resonant modes E and F_2.

order	term in effective Hamiltonian		parameter
	this work	notation in [38]	value
0	H_{ff}^0	T_{ff}^0	$\sqrt{2}$
0	H_{ee}^0	T_{ee}^0	1
2	J^2	$T^{2(0,A_1)}$	1/2
2	$H_{ff}^{1(1,F_1)}$	$-\sqrt{3}\,T_{ff}^{1(1,F_1)}$	$\sqrt{6}/4$
2	$V_{eeee}^{A_1}$	$2\,T_{eeee}^{A_1}$	$-27/16$
2	V_{eeee}^{E}	$\sqrt{2}\,T_{eeee}^{E}$	$9\sqrt{2}/32$
2	$V_{ffff}^{A_1}$	$2\,T_{ffff}^{A_1}$	$-5/6$
2	V_{ffff}^{E}	$\sqrt{2}\,T_{ffff}^{E}$	$521\sqrt{2}/1344$
2	$V_{ffff}^{F_2}$	$2\,T_{ffff}^{F_2}/\sqrt{3}$	$-5\sqrt{3}/96$
2	$V_{efef}^{F_1}$	$T_{efef}^{F_1}/\sqrt{3}$	$15\sqrt{6}/16$
2	$V_{efef}^{F_2}$	$T_{efef}^{F_2}/\sqrt{3}$	$-67\sqrt{6}/336$
4	$H_{ff}^{2(0,A_1)}$	$-\frac{4}{3}\,T_{ff}^{2(0,A_1)}$	$-17\sqrt{2}/32$
4	$H_{ff}^{2(2,E)}$	$\sqrt{2}\,T_{ff}^{2(2,E)}$	$-23/32$
4	$H_{ff}^{2(2,F_2)}$	$\sqrt{3}\,T_{ff}^{2(2,F2)}$	$17\sqrt{6}/64$
4	$H_{ee}^{2(0,A_1)}$	$-\frac{2\sqrt{2}}{\sqrt{3}}\,T_{ee}^{2(0,A_1)}$	$\sqrt{6}/4$
4	$H_{ee}^{2(2,E)}$	$\sqrt{2}\,T_{ee}^{2(2,E)}$	$-3\sqrt{6}/16$
6	$H_{ff}^{3(1,F_1)}$	$-\sqrt{3}\,T_{ff}^{3(1,F_1)}$	$43\sqrt{2}/80$
6	$H_{ff}^{3(3,F_1)}$	$-\sqrt{3}\,T_{ff}^{3(3,F_1)}$	$27\sqrt{15}/160$
6	$H_{ee}^{3(3,A_2)}$	$-T_{ee}^{3(3,A_2)}$	$-7/8$
6	J^4	$T^{4(0,A_1)}$	$-7/60$
6	$R^{4(4,A_1)}$	$T^{4(4,A_1)}$	$-\sqrt{30}/640$

3.6 Parameters of the effective dipole moment

The most important interaction of the vibrating molecule with light is due to the oscillating electric dipole moment M. The ν_3 mode of P_4 is the only active mode in the absorption spectrum because the $q_3^{F_2}$ normal mode is the only distortion of the tetrahedral equilibrium configuration which induces M. In the initial vibrational coordinates of (9) and (11) the vector of the vibrationally induced dipole moment M equals $\mu_{\mathrm{el}}\, q_3^{F_2}$ where μ_{el} is a molecular parameter which depends, among other factors, on the properties of the electronic state.

In the transformed coordinates of the normal form H_{eff} the dipole moment M is represented by a power series in

Table 5. High order anharmonic terms in the effective rovibrational polyad Hamiltonian of the P$_4$ molecule.

order	term in H_{eff}	parameter value
4	$H^{1(1,F_1)}_{efF_1efF_1}$	$-83\sqrt{6}/784+23\sqrt{3}/392$
4	$H^{1(1,F_1)}_{efF_2efF_2}$	$1327\sqrt{6}/784+23\sqrt{3}/392$
4	$H^{1(1,F_1)}_{efF_1efF_2}$	$-933\sqrt{2}/196+23/196$
4	$H^{1(1,F_1)}_{ffEffF_2}$	$107\sqrt{6}/2352$
4	$H^{1(1,F_1)}_{ffF_2ffF_2}$	$-173\sqrt{3}/96$
4	$V_{eeA_1eE.eeA_1eE}$	$-1215\sqrt{2}/2048$
4	$V_{eeEeA_2.eeEeA_2}$	$1971/512$
4	$V_{eeEeA_1.eeEeA_1}$	$-2565/512$
4	$V_{ffF_2fA_1.ffF_2fA_1}$	$6887\sqrt{2}/9216$
4	$V_{ffEfF_1.ffEfF_1}$	$77561\sqrt{6}/37632$
4	$V_{ffA_1fF_2.ffA_1fF_2}$	$57175\sqrt{6}/225792$
4	$V_{ffF_2fF_2.ffF_2fF_2}$	$-819893\sqrt{6}/903168$
4	$V_{ffEfF_2.ffEfF_2}$	$-1657633\sqrt{6}/12644352$
4	$V_{eeEfF_1.eeEfF_1}$	$124949\sqrt{6}/75264$
4	$V_{eeEfF_2.eeA_1fF_2}$	$-445909\sqrt{6}/790272$
4	$V_{eeEfF_2.eeEfF_2}$	$-4548679\sqrt{6}/1580544$
4	$V_{eeA_1fF_2.eeA_1fF_2}$	$3669209\sqrt{6}/1580544$
4	$V_{ffEeE.ffA_1eE}$	$919579\sqrt{2}/225792$
4	$V_{ffA_1eE.ffA_1eE}$	$2400913\sqrt{2}/790272$
4	$V_{ffEeA_1.ffEeA_1}$	$-469711\sqrt{2}/301056$
		$-20755921/3161088$
4	$V_{ffEeA_2.ffEeA_2}$	$-469711\sqrt{2}/301056$
		$+718247/150528$
4	$V_{ffF_2eF_2.ffF_2eF_2}$	$-247675\sqrt{3}/790272$
4	$V_{ffEeE.ffEeE}$	$469711/150528$
		$-2836367\sqrt{2}/3161088$
4	$V_{ffF_2eF_1.ffF_2eF_1}$	$-21827\sqrt{3}/43904$

q, p, and j and is called an effective dipole moment M_{eff},

$$M_{\mathrm{eff}} = \mu_{\mathrm{el}}(M_0 + \epsilon\mathcal{M}_1 + \epsilon^2\mathcal{M}_2 + \ldots),$$

where the series in the brackets is nothing else but the expression of the initial coordinates q_3 in terms of transformed variables $(q_2^E, p_2^E, q_3^{F_2}, p_3^{F_2})$ and $\mathbf{j}$. This expression is given by the Lie exponent constructed from the generator of the normal form transformation [31].

The electric dipole moment in the molecule fixed frame is a 3-vector which transforms (as any other vector) according to the irreducible representation F_2 of the T_d point group and is invariant with respect to time reversal $\mathcal{T}$. This restricts the form of the terms in M_{eff}. Table 6 presents some of the terms in M_{eff} obtained using the same Lie transformation that resulted in our normal form H_{eff}.

Table 6. Principal terms in the effective vibrational electric dipole moment of the P$_4$ molecule.

order	term in M_{eff}	parameter	band
0	$q_3^{F_2}$	1	$0 \to \nu_3$
1	$\left[q_3^{F_2} q_3^{F_2}\right]^{F_2}$	$2^{1/4}/4$	$0 \to 2\nu_3$
1	$\left[p_3^{F_2} p_3^{F_2}\right]^{F_2}$	$2^{-3/4}$	$0 \to 2\nu_3$
1	$\left[q_3^{F_2} q_2^{E}\right]^{F_2}$	$-\sqrt{3}/21$	$0 \to \nu_3{+}\nu_2$
1	$\left[p_3^{F_2} p_2^{E}\right]^{F_2}$	$-2\sqrt{6}/21$	$0 \to \nu_3{+}\nu_2$
2	$\left[p_2^{E} R^{1(1,F_1)}\right]^{F_2}$	$2^{1/4}$	$0 \to \nu_2$
2	$\left[p_3^{F_2} R^{1(1,F_1)}\right]^{F_2}$	0	
2	terms of the type p^2q and q^3		
3	$R^{2(2,F_2)}$	$-2^{3/4}/2^4$	$0 \to 0$
3	terms of the type pqj, q^2p^2, and q^4		
4	$j^2 q_3^{F_2}$	$-49/48$	$0 \to \nu_3$
4	$\left[q_3^{F_2} R^{2(2,F_2)}\right]^{F_2}$	$-49/2^7$	$0 \to \nu_3$
4	$\left[q_3^{F_2} R^{2(2,E)}\right]^{F_2}$	$29\sqrt{6}/2^7$	$0 \to \nu_3$
4	$\left[q_2^{E} R^{2(2,F_2)}\right]^{F_2}$	$19\,2^{1/4}\sqrt{6}/48$	$0 \to \nu_2$
4	terms of the type pq^2j, p^3j, qp^4, q^3p^2, and q^5		

4 Rotational-vibrational relative equilibria

Equilibria of H_{eff} which exist at any arbitrarily small perturbation ϵ, are relative equilibria (RE) or *nonlinear normal modes* of the initial rotation-vibration Hamiltonian H. Many RE of our highly symmetric system can be found using only symmetry arguments [27]. The action of the discrete symmetry group $T_d{\times}\mathcal{T}$ on the reduced phase space $CP_2{\times}CP_1{\times}S_2$ has a number of isolated fixed points [27] which are necessarily stationary points of the reduced Hamiltonian H_{eff}. However, as shown in [27], H_{eff} has several other equilibria which are not fixed but nevertheless exist for any $T_d{\times}\mathcal{T}$ symmetric Morse function H_{eff} on $CP_2{\times}CP_1{\times}S_2$. We also consider such equilibria as RE.

The value of H_{eff} at fixed points of the group action found in [27] gives the energy of RE as function of the three integrals of the reduced system j, n_e, and n_f. Knowing the energy of all RE at given fixed values J, N_e, and N_f we can describe the structure of the energy level multiplet of the corresponding quantum system characterized by quantum numbers J, N_e, and N_f. Note that in the original phase space our relative equilibria are tori; action integrals along appropriate directions on these tori (at fixed energy) give J, N_e, and N_f.

4.1 Analysis of finite symmetries, fixed points

The full symmetry group of our initial Hamiltonian is $T_d{\times}\mathcal{T}$. The symmetry group T_d is originally defined as a group of transformations of the 3-space R_3 with coordinates (x, y, z). Its action is extended symplectically to (p_x, p_y, p_z). The action of $\mathcal{T}$ in (5) is anti-symplectic (changes the sign of the symplectic form). Action of $T_d{\times}\mathcal{T}$ on $CP_2{\times}CP_1{\times}S_2$ is described fully in [27] on the basis of the analysis of the $T_d{\times}\mathcal{T}$ action on the components of the F_2 mode (q_1, q_2, q_3) which transform as (x, y, z), on the E-mode variables, on the angular momentum components, and subsequently on the spaces CP_2, CP_1, and S_2.

We would like to draw attention to the predecessors of [27]. Thus the action of point groups on the rotational sphere S_2 has been analyzed explicitly or implicitly

Table 7. Full stabilizers and number of points in the critical orbit of each type on the CP_2 space. Symmetry operations $C_s \circ \mathcal{T}$ and $C_2 \circ \mathcal{T}$ are denoted as $\mathcal{T}_2$ and $\mathcal{T}_s$. The number of points corresponds to the number of equivalent fixed RE in the case of polyads of the $\nu_3^{F_2}$ mode.

type of orbit	shorthand notation	full stabilizer see [27]	number of points
B, C	S_4	$S_4 \wedge \mathcal{T}_2$	6
B, C	C_3	$C_3 \wedge \mathcal{T}_s$	8
A	S_4	$D_{2d} \wedge \mathcal{T}$	3
A	C_3	$C_{3v} \wedge \mathcal{T}$	4
A	C_s	$C_{2v} \wedge \mathcal{T}$	6

Table 8. Fixed points of the $T_d \times Z_2$ group action on the reduced phase space $CP_2 \times CP_1 \times S_2$ (according to [27]).

a. Stabilizer S_4^z (or C_4), $r_f = \sqrt{N_f}$, $r_e = \sqrt{2N_e}$, $r_j = J$.

point	$\frac{z_1}{r_f}$	$\frac{z_2}{r_f}$	$\frac{z_3}{r_f}$	$\frac{z_4}{r_e}$	$\frac{z_5}{r_e}$	$\frac{j_1}{r_j}$	$\frac{j_2}{r_j}$	$\frac{j_3}{r_j}$
A_1	0	0	$\sqrt{2}$	1	0	0	0	1
A_1'	0	0	$\sqrt{2}$	1	0	0	0	−1
A_2	0	0	$\sqrt{2}$	0	1	0	0	1
A_2'	0	0	$\sqrt{2}$	0	1	0	0	−1
B_1	1	i	0	1	0	0	0	1
B_1'	1	−i	0	1	0	0	0	−1
B_2	1	i	0	0	1	0	0	1
B_2'	1	−i	0	0	1	0	0	−1
C_1	1	i	0	1	0	0	0	−1
C_1'	1	−i	0	1	0	0	0	1
C_2	1	i	0	0	1	0	0	−1
C_2'	1	−i	0	0	1	0	0	1

b. Stabilizer C_3 [111], $r_f = \frac{\sqrt{2N_f}}{\sqrt{3}}$, $r_e = \sqrt{N_e}$, $r_j = \sqrt{3}J$, $\chi = \exp(2\pi \mathrm{i}/3)$.

point	$\frac{z_1}{r_f}$	$\frac{z_2}{r_f}$	$\frac{z_3}{r_f}$	$\frac{z_4}{r_e}$	$\frac{z_5}{r_e}$	$\frac{j_1}{r_j}$	$\frac{j_2}{r_j}$	$\frac{j_3}{r_j}$
A_1	1	1	1	1	i	1	1	1
A_2	1	1	1	1	−i	1	1	1
B_1	1	χ	$\bar{\chi}$	1	i	1	1	1
B_2	1	χ	$\bar{\chi}$	1	−i	1	1	1
C_1	1	χ	$\bar{\chi}$	1	i	−1	−1	−1
C_2	1	χ	$\bar{\chi}$	1	−i	−1	−1	−1

c. Stabilizer C_s^{xy} (or C_2), $r_f = \sqrt{N_f}$, $r_e = \sqrt{2N_e}$, $r_j = J/\sqrt{2}$.

point	$\frac{z_1}{r_f}$	$\frac{z_2}{r_f}$	$\frac{z_3}{r_f}$	$\frac{z_4}{r_e}$	$\frac{z_5}{r_e}$	$\frac{j_1}{r_j}$	$\frac{j_2}{r_j}$	$\frac{j_3}{r_j}$
A_1	1	−1	0	1	0	1	−1	0
A_2	1	−1	0	0	1	−1	1	0

in many studies of classical molecular rotational systems (see Sect. 1). Group action on the reduced space of the 2-oscillator with symmetry, notably of the E-mode vibration of triatomic molecules with three-fold symmetry [15] and others [11] was studied in a similar way. Finally, action of the T_d group on CP_2 was studied in [16] more than a decade ago. Further information can be found in [28].

For an idea of how the group action is found, consider the 2-sphere defined by $j_1^2 + j_2^2 + j_3^2 = 1$ and rotate this sphere about axis j_1. Such an operation has, obviously, two fixed points with $j_1 = \pm 1$. In fact for any rotation we have two fixed points on the sphere. Similarly, for any rotation we consider a point in CP_2 lying on the axis of rotation and a subspace orthogonal to the axis. The former is obviously an isolated fixed point, while the latter is a $CP_1 \sim S_2$ subspace of CP_2 which may contain other symmetric or fixed points. Thus, if we rotate through $2\pi/k$ about axis z_1, we should consider the point $(1, 0, 0)$ and the subspace CP_1 with $z_1 = 0$ and $|z_2|^2 + |z_3|^2 = 1$. In the case $k = 2$, operation C_2 sends (z_2, z_3) to $(-z_2, -z_3)$ which is the same point on CP_1 and therefore the whole $CP_1 \sim S_2$ subspace is C_2-invariant. For higher symmetries $k > 2$ we always have two fixed points on $CP_1 \sim S_2$.

Fixed points of the $T_d \times \mathcal{T}$ action form *orbits* of equivalent points. Relative equilibria (RE) corresponding to different points in the same orbit are equivalent. Orbits are distinguished by their full *stabilizer* [27] listed in the third column of Table 7. Below we use the simplified notation of the T_d group, the alternative O group notation C_4, C_3, C_2' is also popular. In Table 8 each orbit is represented by one fixed point with stabilizer S_4^z, $C_3[111]$ and C_s^{xy} respectively (see [27] for explicit definition of group operations). All other points in the same orbit with conjugated stabilizers can be obtained from the given point using other symmetry operations of T_d, such that for example $S_4^x = R \circ S_4^z \circ R^{-1}$. Of course, the value of the reduced Hamiltonian H_{eff} is the *same* at each of the equivalent points in the orbit.

Orbits of fixed points on $CP_2 \times CP_1 \times S_2$ with stabilizers S_4 and C_3 can be of six types labeled A_1, A_2, B_1, B_2, C_1, C_2. Projection of the A points in the F-mode space CP_2 lies on the rotation axis while such projections of the B or C points lie on the CP_1 subspace of CP_2 orthogonal to this axis; indices 1 and 2 distinguish two different possibilities in the E-mode space. Critical orbits of the T_d action with stabilizer C_s are only of type A. Other possible points with stabilizer C_s (which can be considered as analogs of B and C) are not fixed entirely by symmetry, but lie on the C_s invariant subspace of $CP_2 \times CP_1 \times S_2$ and are not critical (not isolated).

For the example of S_4^z points in Table 8a we list points of type A', B', and C', which are time reversal images of A, B, C. With regard to the T_d group action A and A' represent different orbits because no operation in T_d maps $A \to A'$. With regard to the action of the full group $T_d \times \mathcal{T}$, points of the type A and A' (similarly for B and B', C and C') belong to the same orbit (are equivalent). For the corresponding trajectories of the initial system this means that A and A' is a pair of trajectories which fill the same torus and share the same configuration space image but run in opposite directions.

Table 9. Values of reduced the Hamiltonian H_{eff} on critical orbits, or energy of relative equilibria entirely defined by symmetry. The symmetry of the orbit is indicated by superscripts $^{(2)}$, $^{(3)}$, $^{(4)}$; upper sign in $\pm$ or $\mp$ corresponds to the first point specified by type (B, C) or index $_{1,2}$.

point	order ϵ^2	order ϵ^4 terms q^2J^2	order ϵ^4 terms q^4J	order ϵ^6
$A_1^{(2)}$		$\frac{5}{12}\sqrt{2}N_fJ^2 - \frac{11}{8}N_eJ^2$		$+\frac{1}{80}J^4$
$A_2^{(2)}$		$\frac{5}{12}\sqrt{2}N_fJ^2 - \frac{5}{8}N_eJ^2$		$+\frac{1}{80}J^4$
$A_1^{(4)}$		$\frac{5}{3}\sqrt{2}N_fJ^2 - \frac{1}{4}N_eJ^2$		$-\frac{1}{20}J^4$
$A_2^{(4)}$		$\frac{5}{3}\sqrt{2}N_fJ^2 - \frac{7}{4}N_eJ^2$		$-\frac{1}{20}J^4$
$(B,C)_1^{(4)}$	$\mp\frac{1}{2}N_fJ$	$\frac{11}{48}\sqrt{2}N_fJ^2 - \frac{1}{4}N_eJ^2$	$\mp\frac{107}{2352}\sqrt{2}N_f^2J \pm \frac{11}{8}N_fN_eJ$	$-\frac{1}{20}J^4 \pm \frac{1}{12}N_fJ^3$
$(B,C)_2^{(4)}$	$\mp\frac{1}{2}N_fJ$	$\frac{11}{48}\sqrt{2}N_fJ^2 - \frac{7}{4}N_eJ^2$	$\mp\frac{107}{2352}\sqrt{2}N_f^2J \pm \frac{1949}{392}N_fN_eJ$	$-\frac{1}{20}J^4 \pm \frac{1}{12}N_fJ^3$
$A_{1,2}^{(3)}$		$-N_eJ^2$	$\mp\frac{23}{294}\sqrt{2}N_fN_eJ$	$+\frac{1}{30}J^4 \mp \frac{7}{3}N_eJ^3$
$B_{1,2}^{(3)}$	$-\frac{1}{2}N_fJ$	$+\frac{17}{16}\sqrt{2}N_fJ^2 - N_eJ^2$	$-\frac{2897}{2352}\sqrt{2}N_f^2J + \left(\frac{311}{98} \pm \frac{23}{588}\sqrt{2}\right)N_fN_eJ$	$+\frac{1}{30}J^4 + \frac{7}{3}(N_f \mp N_e)J^3$
$C_{1,2}^{(3)}$	$+\frac{1}{2}N_fJ$	$+\frac{17}{16}\sqrt{2}N_fJ^2 - N_eJ^2$	$+\frac{2897}{2352}\sqrt{2}N_f^2J - \left(\frac{311}{98} \pm \frac{23}{588}\sqrt{2}\right)N_fN_eJ$	$+\frac{1}{30}J^4 - \frac{7}{3}(N_f \mp N_e)J^3$

The number of points in an orbit equals the order of the group $T_d\times\mathcal{T}$ divided by the order of the stabilizer of the orbit. For all critical orbits represented in Table 8 this number of points equals the number of conjugated stabilizers in the T_d group times two. Points on $CP_2\times CP_1\times S_2$ are never invariant with regard to $\mathcal{T}$ because points (j_1, j_2, j_3) on the rotational sphere S_2 are not $\mathcal{T}$-invariant. Therefore, we should always double the number of points to account for $\mathcal{T}$. The number of conjugated subgroups S_4, C_3, and C_s of the T_d group is 3, 4, and 6 respectively (consider axes C_4, C_3, and C_2' of the cube) and consequently orbits with these stabilizers have 6, 8, and 12 points. This fact has a well-known manifestation in rotational energy level spectra in the form of 6, 8, and possibly 12-fold degenerate groups of levels or *clusters* [6–8].

4.2 Energy of fixed relative equilibria

We begin with critical orbits, *i.e.*, isolated fixed points of the $T_d\times\mathcal{T}$ group action on the reduced phase space $CP_2\times CP_1\times S_2$ which are *always* stationary points of H_{eff}. The position of these points on $CP_2\times CP_1\times S_2$ is fixed and the corresponding RE are called *fixed*. The energy of these RE equals the value of H_{eff} at the points in Table 8. It is computed directly after we use Table 3 to express H_{eff} presented in Tables 4 and 5 as function of $(z, \bar{z})$ and (j_1, j_2, j_3). Resulting values of $\mathcal{H}_2$, $\mathcal{H}_4$, and $\mathcal{H}_6$ in (16) are presented in Tables 9 and 10 for each RE in Table 8. The scalar part

$$H_{\text{scalar}} = \sqrt{2}N_f + N_e + \frac{1}{2}\epsilon^2J^2 - \frac{7}{60}\epsilon^6J^4,$$

which is common to all RE, is subtracted from these values. The actual energy thus equals

$$\omega\big(H_{\text{scalar}} + \epsilon^2\mathcal{H}_2 + \epsilon^4\mathcal{H}_4 + \epsilon^6\mathcal{H}_6\big).$$

It is instructive to consider critical orbits in different limiting cases. For pure rotation $N_e = N_f = 0$, $J \neq 0$, orbits A, B, C become indistinguishable and we have 6, 8, and 12 rotational RE with stabilizers C_4, C_3, and C_2 respectively.

In the case of pure E-mode vibrations with $J = N_f = 0$, we come to a 1:1 oscillator with 3-fold symmetry. (Recall that the image of S_4 and C_s in the representation spanned by the E-mode variables is C_2 and C_2'). Other well-known systems of this kind are the Hénon-Heiles oscillator or the E-mode of the triatomic ion H_3^+ [15,14]. There are 8 nonlinear normal modes, denoted in [12] as $\Pi_{7,8}$ (Π_7 is the reversal image of Π_8, both have stabilizer C_3), $\Pi_{1,2,3}$ (stabilizer C_2) and $\Pi_{4,5,6}$ (stabilizer C_2'). In the notation of Table 8 they correspond to $A_{1,2}^{(3)}$, $A_1^{(2)}$, and $A_2^{(2)}$ respectively. (Labels A, B, C, and superscripts $^{(2)}$ and $^{(4)}$ are identical.)

In the case of pure F_2-mode vibrations with $J = N_e = 0$, we have the 27 nonlinear normal modes also initially found in [12]. These modes are illustrated in Figure 8 of [14]. The B and C type RE share the same configuration image shown in the top row of this figure. Modes of the A type are shown in the bottom row. Numbers of equivalent RE are given in Table 7.

Both in the case of pure E mode and F_2 mode vibrations relative equilibria correspond to periodic orbits with action N along the orbit given by N_e and N_f respectively.

Table 10. Values of purely vibrational anharmonic polyad terms of the reduced Hamiltonian $H_{\rm eff}$ on critical orbits corresponding to fixed RE. Upper sign in ± corresponds to the first index in $_{1,2}$.

point	order ϵ^2 terms q^4	order ϵ^4 terms q^6
$A_1^{(2)}$	$-\frac{45}{64}N_e^2 - \frac{643}{2688}N_f^2 + \frac{439}{672}\sqrt{2}N_f N_e$	$+\frac{11089081}{101154816}\sqrt{2}N_f^3 - \frac{1405841}{3161088}N_e N_f^2 + \frac{4945895}{3161088}\sqrt{2}N_f N_e^2 - \frac{6345}{4096}N_e^3$
$A_2^{(2)}$	$-\frac{45}{64}N_e^2 - \frac{643}{2688}N_f^2 + \frac{19}{224}\sqrt{2}N_f N_e$	$+\frac{11089081}{101154816}\sqrt{2}N_f^3 + \frac{930283}{526848}N_e N_f^2 + \frac{450453}{351232}\sqrt{2}N_f N_e^2 + \frac{2727}{4096}N_e^3$
$A_1^{(4)}$	$-\frac{45}{64}N_e^2 - \frac{13}{672}N_f^2 - \frac{67}{336}\sqrt{2}N_f N_e$	$-\frac{18911}{6322176}\sqrt{2}N_f^3 - \frac{185755}{1580544}N_e N_f^2 - \frac{221411}{395136}\sqrt{2}N_f N_e^2 - \frac{6345}{4096}N_e^3$
$A_2^{(4)}$	$-\frac{45}{64}N_e^2 - \frac{13}{672}N_f^2 + \frac{15}{16}\sqrt{2}N_f N_e$	$-\frac{18911}{6322176}\sqrt{2}N_f^3 + \frac{23747}{25088}N_e N_f^2 + \frac{1}{256}\sqrt{2}N_f N_e^2 + \frac{2727}{4096}N_e^3$
$B_1^{(4)}\ C_1^{(4)}$	$-\frac{45}{64}N_e^2 + \frac{451}{2688}N_f^2 + \frac{439}{672}\sqrt{2}N_f N_e$	$-\frac{1869407}{101154816}\sqrt{2}N_f^3 + \frac{2566355}{3161088}N_e N_f^2 + \frac{4945895}{3161088}\sqrt{2}N_f N_e^2 - \frac{6345}{4096}N_e^3$
$B_2^{(4)}\ C_2^{(4)}$	$-\frac{45}{64}N_e^2 + \frac{451}{2688}N_f^2 + \frac{19}{224}\sqrt{2}N_f N_e$	$-\frac{1869407}{101154816}\sqrt{2}N_f^3 - \frac{556987}{263424}N_e N_f^2 + \frac{450453}{351232}\sqrt{2}N_f N_e^2 + \frac{2727}{4096}N_e^3$
$A_1^{(3)}\ A_2^{(3)}$	$+\frac{9}{32}N_e^2 - \frac{5}{16}N_f^2 + \frac{31}{84}\sqrt{2}N_f N_e$	$-\frac{235}{1536}\sqrt{2}N_f^3 + \frac{18337}{24696}N_e N_f^2 - \frac{962375}{1580544}\sqrt{2}N_f N_e^2 - \frac{297}{512}N_e^3$
$B_{1,2}^{(3)}\ C_{1,2}^{(3)}$	$+\frac{9}{32}N_e^2 + \frac{127}{1344}N_f^2 + \frac{31}{84}\sqrt{2}N_f N_e$	$+\frac{9783049}{2^{13}3^2 7^3}\sqrt{2}N_f^3 - X_\pm N_e N_f^2 - \frac{962375}{2^9 3^2 7^3}\sqrt{2}N_f N_e^2 - \frac{297}{2^9}N_e^3$
		where $X_\pm = -\left(\frac{29\times 62053}{2^{10}3^2 7^3} \pm \frac{11\times 42701}{2^{11}3^2 7^2}\sqrt{2}\right)$

The series for the energy $H_{\rm eff}(N) = h$ can be inverted to obtain the action as a function of energy $N(h)$.

4.3 Stability of fixed relative equilibria

To complete the characterization of relative equilibria we should specify their stability and, possibly, indicate if this stability can change when the parameters of the system, such as N_f, N_e, and J, vary. Full stability analysis requires additional mathematical tools and can be quite complicated (see [27]). Here we only study one simple, important case of the vibrational F_2 mode RE $A^{(4)}$.

The F_2 mode reduced Hamiltonian $\mathcal{H}_{\rm nf}$ is obtained from the general normal form in Tables 4 and 5 when J and N_e are set to 0. This Hamiltonian describes a reduced 1:1:1 oscillator system with symmetry $T_d{\times}\mathcal{T}$. The energy of the $A^{(4)}$ relative equilibrium of this system is obtained in the same way from the general expression in Tables 9 and 10. To determine the linear stability of this RE we use a simple method which resembles the Poincaré surface of section construction in the original phase space C_3 with coordinates (z_1, z_2, z_3) and conjugated momenta $(\bar{z}_1, \bar{z}_2, \bar{z}_3)$. One of the three $A^{(4)}$ equilibria on CP_2 (see Tab. 8a) has coordinates

$$z_1 = z_2 = 0, \quad z_3 = \sqrt{2N_f}.$$

Near this point on CP_2 we can use the map

$$(z_1, z_2, z_3)\big|_{CP_2} \to \left(z_1, z_2, \sqrt{2N_f - z_1^2 - z_2^2}\right),$$

which brings us from CP_2 to a complex plane C_2 with canonical coordinates $(z_1, \bar{z}_1)$ and $(z_2, \bar{z}_2)$ [40]. We apply this map to $\mathcal{H}_{\rm nf}$ and use a power series expansion in $(z_1, \bar{z}_1, z_2, \bar{z}_2)$. The resulting Hamiltonian describes small oscillations about the RE. The matrix of the linear part of the flow of the corresponding vector field $X_{\mathcal{H}}$ has eigenvalues $(\omega, -\omega, \omega, -\omega)$ where

$$\omega = -1.6227\,\epsilon^2 n^2 + 0.6825\,\epsilon^4 n^3 + ...$$

We conclude that the $A^{(4)}$ relative equilibrium of the F_2 mode vibrations is *unstable* and has the signature $(-{+}{-}{+})$. This has an interesting consequence. Assuming that $\mathcal{H}_{\rm nf}$ is a Morse function on CP_2 and using the requirements for such functions in the presence of the $T_d{\times}\mathcal{T}$ group action we can now show [27] that there are additional RE which do not lie on the critical orbits (fixed points) of the group action. In other words, the vibrational Hamiltonian which describes the $\nu_3(F_2)$ mode polyads of P_4 on the basis of our model potential (11) is *not* of the simplest possible kind and has more than necessary minimum of RE.

We should further remark that extending the above analysis to the full reduced phase space $CP_2{\times}CP_1{\times}S_2$, *i.e.*, to the case of nonzero J and N_e, is straightforward but surely more cumbersome. Vibrational RE of the F_2 mode system can be continued when J and N_e are sufficiently small compared to N_f. Some of these RE bifurcate at larger J and N_e. When going towards the large J limit these bifurcations can be considered as part of the rotation-vibration re-coupling process.

4.4 Relative equilibria on non-critical orbits

We have seen in the previous section that our model for the ν_3 mode vibrational Hamiltonian has relative equilibria on non-critical orbits of the $T_d{\times}\mathcal{T}$ group action on

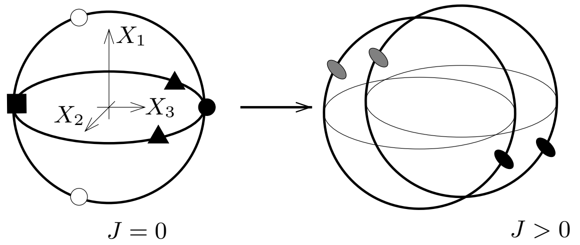

Fig. 5. C_s invariant sphere in the CP_2 subspace when $J = 0$ (left) and two correlating C_s invariant spheres in the $CP_2 \times S_2$ space when $J > 0$ (right). Black disk, square, and triangles denote critical orbits and corresponding vibrational RE of type $A^{(2)}$, $A^{(4)}$, and two RE of type $A^{(3)}$ respectively. White disks mark the position of the additional pair of equivalent vibrational RE. Black and grey ovals on the right denote four additional vibration-rotation RE. Bold lines represent one-dimensional strata.

the reduced phase space CP_2. Analysis of this action on the rotation-vibration reduced phase space $CP_2 \times CP_1 \times S_2$ and application of Morse theory show that any reduced Hamiltonian H_{eff} *always* has stationary points which do not lie on critical orbits (*i.e.*, are not fixed RE). The idea of the proof [27] is to verify that Morse theory requirements are satisfied on all invariant subspaces of the $T_d \times \mathcal{T}$ group action on CP_2 and $CP_2 \times CP_1 \times S_2$. The six C_s-invariant 2-spheres $S_2^{C_s}$ turn out to be of primary interest.

In the pure F_2 mode system ($J = N_e = 0$) the action of $T_d \times \mathcal{T}$ on $S_2^{C_s}$ has four fixed points which correspond to relative equilibria $A^{(2)}$, $A^{(4)}$ (studied in Sect. 4.3) and a pair of $A^{(3)}$. With rotation taken into account ($J > 0$) each of the six C_s invariant spheres on CP_2 lifts to two equivalent spheres in $CP_2 \times S_2$ related by time reversal $\mathcal{T}$ (see Fig. 5). No fixed points (no critical orbits) of the group action and therefore no fixed RE listed in Table 8 remain on the 12 spheres. Finally, with the E-mode also taken into account ($N_e > 0$) we have 24 equivalent C_s spheres in $CP_2 \times CP_1 \times S_2$ with no critical orbits on them.

The C_s symmetry operation is symplectic and $S_2^{C_s}$ are dynamically invariant subspaces of $CP_2 \times CP_1 \times S_2$. Dynamics on $S_2^{C_s}$ is given by the flow of $H_{\text{eff}}^{C_s}$ which is the reduced Hamiltonian H_{eff} restricted on $S_2^{C_s}$ and which we assume to be a Morse function. By Morse theory requirements, $H_{\text{eff}}^{C_s}$ *must* have at least two stationary points on $S_2^{C_s}$, a maximum and a minimum, which constitute the total of 48 additional rotation-vibration RE.

In the rest of this section we consider RE on non-critical orbits in the two important limiting cases, the ν_3 polyads with $J = N_e = 0$ and fast rotational states where $J \gg N_f$ and $J \gg N_e$. These cases correspond to the left and right part of Figure 5.

4.4.1 C_s invariant subspace of CP_2 and $CP_2 \times CP_1 \times S_2$

We consider one of the C_s-invariant spheres with stabilizer C_s^{xy}. Operation C_s^{xy} acts on the rotational phase space S_2 as rotation through π about the diagonal line in the (j_1, j_2) plane. Rotational coordinates are, therefore, fixed

$$j_3 = 0, \quad \text{and} \quad j_1 = -j_2 = \pm J/\sqrt{2}.$$

Action of C_s on the E-mode space CP_1 amounts to a similar rotation; the E-mode coordinates are

$$v_1 = v_3 = 0, \quad \text{and} \quad v_2 = \pm\tfrac{1}{2} N_e,$$

or in terms of complex variables

$$(z_4, z_5) = \left(\sqrt{2N_e}, 0\right) \quad \text{or} \quad \left(0, \sqrt{2N_e}\right).$$

On the F_2-mode space CP_2 the image of the operation C_s^{xy} is a C_2 rotation about the axis orthogonal to the $z_1 = z_2$ (*i.e.*, $x = y$) plane. The invariant subspace $CP_1 \subset CP_2$ lies in the $z_1 = z_2$ plane and can be described using two complex coordinates (ζ, z_3) where $\zeta = (z_1 + z_2)/\sqrt{2}$ and, of course,

$$\frac{1}{2}(\zeta\bar{\zeta} + z_3\bar{z}_3) = N_f.$$

4.4.2 Poisson structure of the C_s restricted system

Equations of motion on the C_s invariant subspace $CP_1 \sim S_2$ (see [27]) are Euler-Poisson equations for the angular momentum components

$$(X_1, X_2, X_3) = \frac{1}{4}\left(\mathrm{i}\zeta\bar{z}_3 - \mathrm{i}z_3\bar{\zeta},\ \zeta\bar{z}_3 + z_3\bar{\zeta},\ \zeta\bar{\zeta} - z_3\bar{z}_3\right),$$

which generate the Poisson algebra $\mathcal{P}(X_1, X_2, X_3)$ with the bracket

$$\{X_i, X_j\} = \epsilon_{ijk} X_k,$$

and the Casimir

$$X_1^2 + X_2^2 + X_3^2 = \left(\frac{N_f}{2}\right)^2.$$

Obviously, $\mathcal{P}$ is the Lie algebra so(3). The last equation can be used to represent $S_2^{C_s}$ in the ambient space R_3 with coordinates (X_1, X_2, X_3).

4.4.3 Residual group action and Morse theory

Position of the RE on $S_2^{C_s}$ can be specified more precisely if we account for the nontrivial residual action of the symmetry group $T_d \times \mathcal{T}$ on this space [27]. In the purely vibrational system we have two symmetry operations which map $S_2^{C_s}$ into itself, the time reversal $\mathcal{T}$ and $\mathcal{T}_2$ which is a combination of $\mathcal{T}$ and rotation C_2 about one of the axes 1, 2, or 3 (*i.e.*, axes (x, y, z) corresponding to axes S_4). Any point with nonzero rotational coordinates (j_1, j_2, j_3) is moved by the $\mathcal{T}$ operation and the latter cannot be considered in the full rotation-vibration system. (In fact

$\mathcal{T}$ maps one $S_2^{C_s}$ space into another with rotational coordinates $(-j_1, -j_2, -j_3)$.) In our example with stabilizer C_s^{xy}, the particular $\mathcal{T}_2$ operation is $C_2^z \circ \mathcal{T}$ (to verify compute $C_2^z \circ \mathcal{T}(j_1, j_2) = C_2^z(-j_1, -j_2) = (j_1, j_2)$). This operation sends (X_1, X_2, X_3) to $(X_1, -X_2, X_3)$. The time reversal operation $\mathcal{T}$ changes the sign of X_1.

Operations $\mathcal{T}$ and $\mathcal{T}_2$ generate a group of order four whose action on $S_2^{C_s}$ in the F_2-mode reduced phase space CP_2 is identical to that of the point group C_{2v} on a sphere in the ambient 3-space with coordinates (X_1, X_2, X_3). The two fixed points of this action correspond to vibrational RE $A^{(2)}$ and $A^{(4)}$ shown in Figure 5, left. The action has two invariant one-dimensional circles (which are intersections of the two symmetry planes and the sphere). Action of the C_3 operation on CP_2 adds a pair of equivalent fixed points $A^{(3)}$ which lie on the $X_1 = 0$ circle of $S_2^{C_s}$ and constitute one orbit of the $\mathcal{T}_2$ operation.

In the full rotation-vibration system, the $X_1 = 0$ circle is no longer an invariant subspace of $S_2^{C_s}$ which has no fixed points of the $T_d \times \mathcal{T}$ group action. When $J > 0$, the C_s restricted reduced Hamiltonian $H_{\text{eff}}^{C_s}$ is no longer $\mathcal{T}$-invariant but it remains $\mathcal{T}_2$-invariant and it should have (at least) two stationary points on the $\mathcal{T}_2$-invariant circle where $X_2 = 0$ (see Fig. 5, right). Position of these points depends on the concrete Hamiltonian H_{eff} and is a function of integrals N_f, N_e, and J.

4.4.4 Vibrational RE in the limit $J = N_e = 0$

The stability analysis of the $A^{(4)}$ relative equilibrium in Section 4.3 indicated that our model of the $\nu_3(F_2)$ mode vibrations of P$_4$ has additional RE. *A priori* we cannot know the position of these RE on the reduced phase space CP_2. Comparison of the energies and stability of all fixed RE can help reducing the number of possibilities. A definitive answer is obtained by a direct study of the reduced Hamiltonian function restricted to various invariant subspaces of CP_2. It turns out that for our model additional stationary points lie on the C_s invariant sphere.

After restricting H_{eff} to the C_s^{xy} invariant sphere as described in Section 4.4.1 and setting J and N_e to 0 we obtain

$$\mathcal{H}(X_1, X_3) = \sqrt{2} N_f$$
$$+ \left(\frac{547}{2^4 21} X_1^2 - \frac{197}{2^7 7} X_3 N_f + \frac{591}{2^7 7} X_3^2 - \frac{3163}{2^9 21} N_f^2 \right) \epsilon^2 + ...$$

The set of the stationary points of $\mathcal{H}(X_1, X_3)$ is defined qualitatively by the quartic anharmonic terms V_{ffff} of order ϵ^2. The plot of this function shown in Figure 6 confirms that the two additional RE lie on the $\mathcal{T}_2$-invariant circle ($X_2 = 0$). These RE are mapped into each other by time reversal symmetry $\mathcal{T}$. To find these relative equilibria we restrict equations of motions

$$\dot{X} = \{X, \mathcal{H}(X_1, X_3)\} = 0,$$

to the $X_2 = 0$ circle and solve the sole remaining equation

$$\dot{X}_2 = \left(\frac{197}{896} N_f + \frac{2603}{1344} X_3 \right) X_1 \epsilon^2 + ... = 0$$

for $X_3 \approx 0$ taking into account that

$$X_1 = \pm \sqrt{\left(\tfrac{1}{2} N_f\right)^2 - X_3^2}.$$

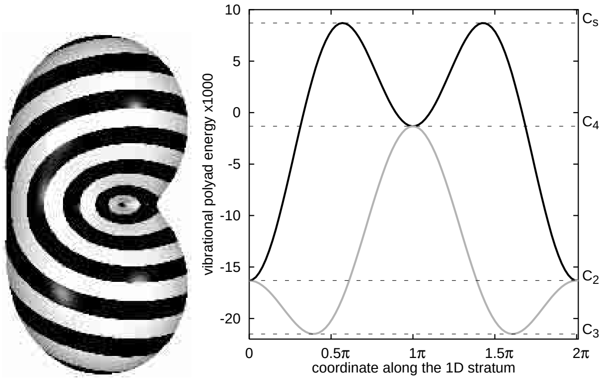

Fig. 6. Normal form H_{eff} with $J = 0$, $N_e = 0$, and $N_f = 10$ restricted to the C_s invariant sphere in the CP_2 space; the value of ϵ is taken from (19b). The function $H_{\text{eff}}^{C_s}$ is shown on the left as a surface in the ambient 3-space with coordinates (X_1, X_2, X_3). Orientation of axes and position of RE corresponds to Figure 5. Black and white stripes represent arbitrarily spaced constant level sets of $H_{\text{eff}}^{C_s}$. The value of $H_{\text{eff}}^{C_s}$ on the one dimensional strata $X_1 = 0$ (lower trace) and $X_2 = 0$ (upper trace) is shown on the right. Dashed lines give the energy of RE located on the C_s invariant sphere when $J = 0$.

The solution obtained by Newton's iteration

$$\arctan\left(\frac{X_3}{|X_1|}\right)\frac{\pi}{180} = -13.123 + 61.581\epsilon^2 N_f + ...$$

shows how the stationary point moves slowly along the $\mathcal{T}_2$ invariant circle as the value of the polyad integral N_f increases. At this point the Hamiltonian $\mathcal{H}(X_1, X_3)$ attains its maximum

$$\sqrt{2} N_f (1 + 0.088597\,\epsilon^2 N_f + 0.180735\,\epsilon^4 N_f^2 + ...)$$

which gives the energy of the additional RE.

4.4.5 Rotation-vibration relative equilibria for $J \gg N$

Additional rotation-vibration RE also lie on the $\mathcal{T}_2$ invariant circle in the $S_2^{C_s}$ subspace of $CP_2 \times CP_1 \times S_2$ (see Fig. 5, right). Again we restrict our H_{eff} to the C_s^{xy} invariant sphere (by setting $z_1 = z_2$), express it as a function of (X_1, X_2, X_3) or in fact of (X_1, X_3) only, and solve the equations for stationary points

$$\dot{X}_2 = \{X_2, H_{\text{eff}}^{C_s}\} = 0, \quad X_2 = 0, \quad X_3^2 + X_1^2 = \left(\frac{N_f}{2}\right)^2.$$

With quartic (and higher) anharmonic terms included in H_{eff} these equations for RE are strongly nonlinear because, contrary to the purely vibrational case, powers of ϵ

do not reflect degrees in X. Such equations can in general be solved only numerically.

We can simplify the general case by assuming that excitation of mode F_2 is small, *i.e.*, that N_f and hence $|X|$ are small (compared to J). We will also make a similar assumption for the E mode. This important limit corresponds to the case of spectroscopic description of the rotational structure of the fundamental states $\nu_3^{F_2}$ and ν_2^{E}, and the combination state $\nu_3^{F_2} + \nu_2^{E}$. Neglecting all terms in $H_{\text{eff}}^{C_s}$ of degree in (N_f, X_1, X_3) and N_e larger than 1 we obtain the Hamiltonian $\mathcal{H}^{C_s}$ which is linear in X,

$$\mathcal{H}^{C_s} = b(J)X_1 - a(J)X_3 + c(J, N_f, N_e) \approx H_{\text{eff}}^{C_s}, \quad \text{(17a)}$$

with coefficients

$$a = -\frac{5\sqrt{2}}{4}\epsilon^4 J^2, \quad b = -\epsilon^2 J + \frac{85}{24}\epsilon^6 J^3, \quad \text{(17b)}$$

and an additive constant

$$c = N_e + \sqrt{2}N_f + \frac{1}{2}\epsilon^2 J^2 + \left(\frac{41}{48}\sqrt{2}N_f - \frac{5}{8}N_e\right)\epsilon^4 J^2 - \frac{5}{48}\epsilon^6 J^4. \quad \text{(17c)}$$

(The first three terms in (17c) come, obviously, from the harmonic oscillator H_0 and rigid body rotator.) The solution of the linear equation $\dot{X}_2 = 0$ obtained for (17a),

$$(X_1, X_2, X_3) = \pm\frac{N_f}{2\sqrt{b^2 + a^2}}(b, 0, -a),$$

was used in [22] and is discussed in more detail in [27]. Since $a(J)$ and $b(J)$ depend differently on J the two RE move along the $\mathcal{T}_2$ invariant circle. When J is small $b \gg a$ and the RE stay near the point $X_3 = 0$, at large J they approach $X_1 = 0$. Their energies are

$$\pm\frac{N_f}{2}\sqrt{b(J)^2 + a(J)^2} + c(J, N_f, N_e). \quad \text{(18)}$$

5 Rotational structure of vibrational states

The normal form H_{eff} in Tables 4 and 5 provides a model description of the vibration-rotation dynamics of the P_4 molecule. In order to understand whether the model works (at least qualitatively) we should compare our classical description with quantum states. Such comparison is based on the known classical–quantum correspondence formulae for the three integrals of motion, N_f, N_e, and J, and dynamical variables $(z, \bar{z})$ and (j_1, j_2, j_3) which are summarized in Table 11.

In certain cases, however, especially for low vibrational excitations, it is interesting to replace classical actions n_f and n_e for quantum numbers N_f and N_e without the Maslov index correction ($\frac{3}{2}$ and 1 respectively). In particular, when our general expressions are restricted to contributions of the terms which are at most quadratic in $(z, \bar{z})$, *i.e.*, the terms which are normally used by spectroscopists to describe phenomenologically the fundamental states $\nu_3^{F_2}$ ($N_f = 1$, $N_e = 0$) and ν_2^{E} ($N_f = 0$, $N_e = 1$) as isolated states, substitution of $n_f = 1$ and $n_e = 1$ reproduces *exactly* the semi-quantum rotational energy surfaces discussed in Section 1.1.

Table 11. Quantum-classical correspondence formulae used in the analysis of the rotation-vibration Hamiltonian H_{eff}.

classical	quantum
J	$\sqrt{J(J+1)} \approx J + \frac{1}{2}$
N_f	$N_f + \frac{3}{2}$
N_e	$N_e + 1$
$(z, \bar{z})$	$\sqrt{2}(a, a^+)$
$j_1 = J\cos\theta$	J_1
$j_2 = J\sin\theta\cos\varphi$	J_2
$j_3 = J\sin\theta\sin\varphi$	J_3

We can construct a quantum analogue of H_{eff} using Tables 4 and 5, compute quantum energies, and compare them, if possible, with experimental data. Quantum calculations can be readily done using the STDS programs [41] once the correspondence of the terms in H_{eff} and quantum operators in [38,41] is established. We can also take expressions for the energies of rotation-vibration RE (Tabs. 9 and 10), replace N_f, N_e, and J for their quantum analogues (Tab. 11) and consider the qualitative structure (*e.g.*, bands, clusters of rotational states, sequences of clusters, etc.) of the rotation-vibration energy level spectrum. In both cases, we need to determine first the values of the two "adjustable" parameters of our model, ω and ϵ, *i.e.*, the strength of the atom–atom bond and the equilibrium geometry. This is done in Section 5.2.1.

5.1 The ground state of P_4

The ground state constants of P_4 are computed in [29] from the energies of purely rotational RE. The main qualitative result of this computation is the correct relation $E_{C_3} > E_{C_2} > E_{C_4}$ of the energies of the three rotational RE which is defined by the sign of the parameter of the principal tetrahedral splitting term $R^{4(4,A_1)}$ of the effective ground state rotational Hamiltonian. For the same one-parameter model we use presently in (11) the ground state constants are given in equation (31) of [29], where the dimensionless smallness parameter ϵ' is related to our ϵ in (15d) as

$$2\epsilon' = \left(KmR^4\right)^{-1} = \epsilon^4.$$

It follows from (15f) that $B_0\,\epsilon' = \omega\epsilon^6/4$ and that the main tetrahedral splitting constant in equation (31) of [29] equals

$$t^{4(4,A_1)} = -\frac{\sqrt{15}}{4\sqrt{2}}D_t = -\frac{\sqrt{15}}{4\sqrt{2}}B_0\frac{\epsilon'}{20} = -\frac{\sqrt{30}}{640}\,\omega\epsilon^6,$$

which matches our result in Table 4. The scalar constants in [29] are not reproduced entirely in Table 4 because the totally symmetric "breathing" mode q^{A_1} is excluded in our present study.

5.2 The ν_3 vibrational mode and its overtones

5.2.1 The $\nu_3^{F_2}$ fundamental state

The energy level structure of the $\nu_3^{F_2}$ fundamental state ($N_f = 1, N_e = 0$) of P_4 was reconstructed by Boudon *et al.* [23] using an effective phenomenological Hamiltonian H_{eff} with parameters fitted to experimental data. Our model in Table 4 also predicts the values of the parameters in

$$\begin{aligned} H_{\text{eff}} &= \omega\sqrt{2}\,H^0_{ff} + \omega H^0_{ee} + \frac{\omega}{2}\epsilon j^2 + \frac{\sqrt{6}\,\omega}{4}\epsilon H^{1(1,F_1)}_{ff} + ..., \\ &= \nu_f T^0_{ff} + \nu_e T^0_{ee} + B\,J^2 + t^{1(1,F_1)}_{ff} T^{1(1,F_1)}_{ff} + ... \end{aligned}$$

Here the spectroscopic notation of [23] is used in the second row, B is the ground state rotational constant, ν_E and ν_F are frequencies. Comparing coefficients in front of j^2 and H^0_{ff} to those fitted to experimental data in [23] we find

$$\omega = \frac{\nu_{F_2}}{\sqrt{2}}, \quad \epsilon^2 = -\frac{4}{3}\frac{t^{1(1,F_1)}}{\nu_{F_2}} = \frac{2B}{\omega}, \tag{19a}$$

which gives the numerical values

$$\omega \approx 329.63, \quad \epsilon \approx 0.02617. \tag{19b}$$

We can now substitute (19b) in the expressions of Table 9 and plot the energy–momentum diagram of relative equilibria of P_4 shown in Figure 7. In this figure we used $n_f = 1$ for a simpler comparison with the data of [23].

It can be seen that our model reproduces correctly the qualitative structure of each of the three branches of the ν_3 state. In the upper and lower branches of ν_3 we have $E_{C_3} > E_{C_2} > E_{C_4}$ while in the central branch $E_{C_4} > E_{C_2} > E_{C_3}$. Internal splitting of the branches is also reproduced to an extent and sixth order of the normal form brings further improvement (see Fig. 7). The discrepancy in the overall J-dependence of the predicted RE energies is at least partially related to our neglecting the totally symmetric mode $\nu_1^{A_1}$, *i.e.*, setting q^{A_1} and p^{A_1} in the initial rotation-vibration Hamiltonian in equations (9) and (11) to zero. More improvement is likely if an anharmonic bond potential or a Morse potential (such as in Sect. 1.4) is used. Our complete classical model reproduces rotational structure of all vibrational polyads. In the $J = 0$ limit, rovibrational relative equilibria become vibrational relative equilibria which describe the internal structure of higher vibrational polyads with $N_f \gg 1$. This structure does not show up at $N_f = 1$ where the $\nu_3^{F_2}$ fundamental state is simply a triply degenerate quantum level.

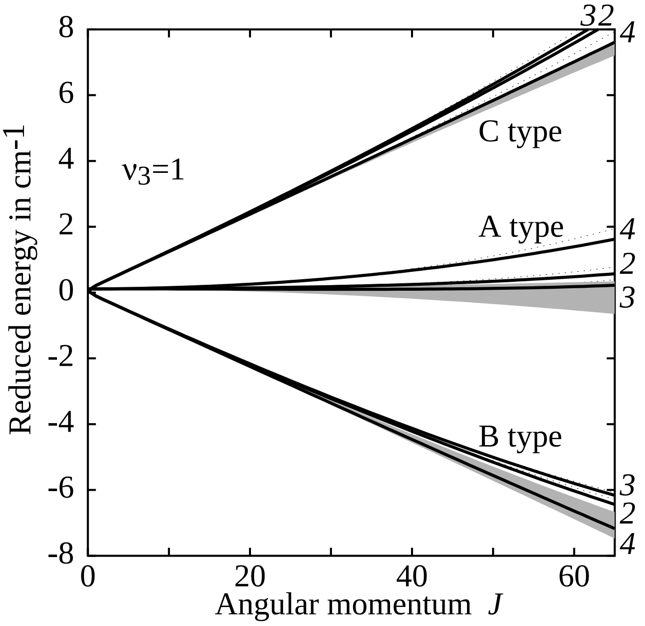

Fig. 7. Relative equilibria (RE) with $N_f = 1$ and $N_e = 0$ and the structure of the $\nu_3^{F_2}$ fundamental state of the P_4 molecule. Bold lines show RE energies obtained for our model in Table 9; dotted lines show the same energies truncated at order ϵ^4; grey shaded area represents quantum energy levels of P_4 shown in Figure 1 according to [23]. In this and subsequent figures, energies are plotted without the scalar term $H_{\text{scalar}}(J)$. The type of RE (A, B, and C) and symmetry index ($k = 2, 3, 4$) correspond to the notation $A^{(k)}$, $B^{(k)}$, $C^{(k)}$ of Tables 8 and 9, and equation (18).

5.2.2 The $2\nu_3$ overtone

The $2\nu_3^{F_2}$ state of P_4 has not yet been observed experimentally. It has three vibrational components of respective symmetries A_1, E and F_2. Only the F_2 component is active in the absorption spectrum. Our model in Table 4 predicts that the energies of the three components at $J = 0$ increase in the order A_1, F_2, E as shown by the leftmost levels in the zoomed part of Figure 8. The splitting at $J = 0$ is due to the quartic terms V_{efef} of order ϵ^2. It quickly gives way to the Coriolis splitting of order $\epsilon^2 J$ when J increases. The global structure at large J is that of a fivefold vibrational level $E + F_2$ whose five rotational branches are superimposed on the single branch of the A_1 component (see Fig. 8).

We can see in Figure 8 that the above energy level spectrum is well represented by the RE energies. The correspondence between the quantum branches and the RE is, however, more complicated. Branches with maximum and minimum energy and part of the central branch can be considered as composed of states which tend to localize near single RE's. Localization in other branches is likely to involve several different kinds of RE at once (*e.g.*, localization near a 2-torus). Further analysis of our prediction for $2\nu_3$ shows that the internal structure of the upper and lower branches of $2\nu_3$ changes qualitatively

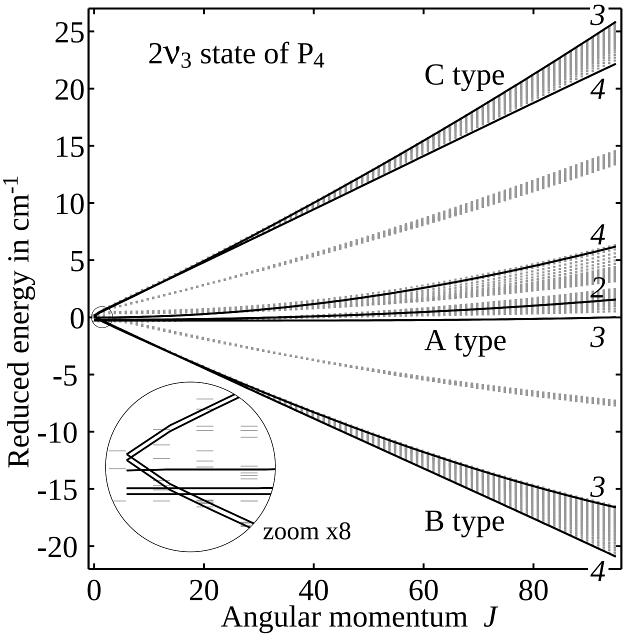

Fig. 8. Relative equilibria (RE) with $N_f = 2$ and $N_e = 0$ and the structure of the rotation-vibration levels of the $2\nu_3$ state of P_4. Bold lines show energies of fixed RE in Table 9; grey bars represent quantum energy levels computed using the Hamiltonian $H_{\rm eff}$ in Table 4 without the scalar terms in $H_{\rm scalar}(J)$. The type A, B, and C and symmetry index $k = 2, 3, 4$ correspond to the RE notation $A^{(k)}$, $B^{(k)}$, $C^{(k)}$ in Tables 8 and 9.

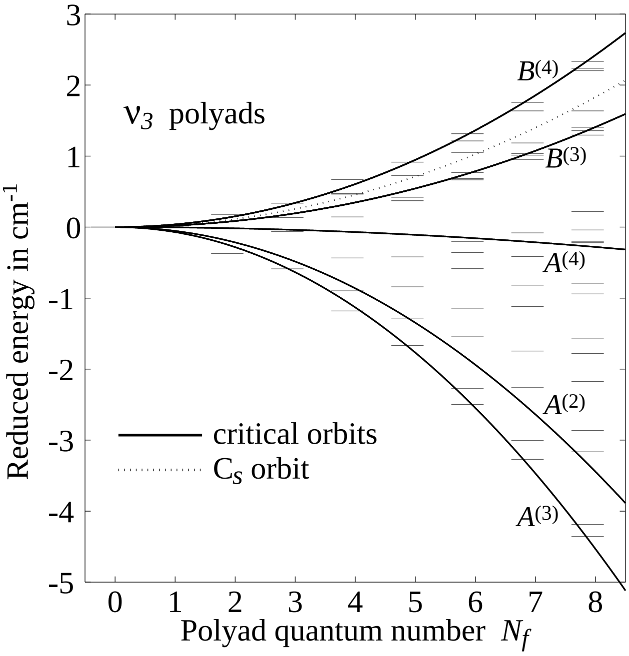

Fig. 9. Energy of the relative equilibria of P_4 corresponding to the critical points of the $T_d \times \mathcal{T}$ action on CP_2 (solid line), additional RE on the C_s invariant sphere (dotted line) and the structure of the ν_3 polyads predicted using the quantized 4th order normal form in Table 4. The notation follows Tables 8 and 9.

Table 12. Quasidegenerate 4-fold and 6-fold states (clusters) at the maximum and minimum energy of the ν_3-mode polyads of P_4 predicted using the quantized 4th order normal form in Table 4. Compare to the whole energy level spectrum in Figure 9. Reduced energies of quantum levels and relative equilibria are in cm^{-1}.

N_f	6	7	8
$B^{(4)}$	**1.36**	**1.85**	**2.42**
6 fold	1.32 E 1.21 F_2 1.05 A_2	1.76 F_2 1.64 F_1	2.33 A_1 2.23 F_1 2.20 E
	⋮	⋮	⋮
4 fold	−2.27 F_2 −2.50 A_1	−3.01 A_1 −3.27 F_2	−4.19 F_2 −4.36 A_1
$A^{(3)}$	**−2.55**	**−3.47**	**−4.53**

near $J \approx 15$ when rotation-vibration terms of order $\epsilon^2 J^2$ outweigh purely vibrational splitting of order ϵ^2 and the energies of $(B,C)^{(4)}$ and $(B,C)^{(3)}$ equilibria change places so that at larger J both branches have $E_{C_3} > E_{C_4}$, *i.e.*, just as in the ν_3 state.

5.2.3 Higher polyads of the $\nu_3^{F_2}$-mode

In the previous paragraphs, we considered two ν_3-mode states of P_4 with comparatively high rotational excitation, *i.e.*, with $J \gg N$. The purely vibrational limit with $N_e = J = 0$ can also be described using the same general normal form $H_{\rm eff}$ in Tables 4 and 5. Characterization of the vibrational polyads of the $\nu_3^{F_2}$-mode follows Section 3 of [14] and [16,17]. This is a higher dimensional generalization of the previous work on 1:1 and 1:2 resonant systems in [11,42].

Most of the analysis of the RE system of the ν_3 mode is done in Sections 4.3 and 4.4.4 where we complete the list of RE of this system. The energies of fixed RE are given in Tables 9 and 10; the energy of the additional RE on the C_s-invariant sphere is obtained in Section 4.4.4. In Figure 9 we plot these energies as function of the ν_3 polyad number N_f with $J = N_e = 0$. We compare them to quantum levels computed using the quantized normal form of order four. (To simplify the comparison we use $n_f = N_f$ instead of the quantum formula in Tab. 11.) We find 6-fold and 4-fold quasi-degenerate vibrational levels near the maximum and minimum energy of each polyad which correspond to the states localized near $(B,C)^{(4)}$ and $A^{(3)}$ relative equilibria. Table 12 gives positions of extremal vibrational clusters corresponding to the $C_{3v} \wedge \mathcal{T}$ ($A^{(3)}$-type) and $S_4 \wedge \mathcal{T}_2$ $B^{(4)}$-type) critical orbits for $N_f = 6, 7, 8$. We can see in Figure 9 that even at such low N_f these extremal clusters are well pronounced. Their width is small compared to the separation from the rest of the spectrum. Detailed analysis of the level structure at intermediate polyad energies is beyond the scope of this paper.

5.3 The ν_2 vibrational mode and its overtones

Unlike the $\nu_3^{F_2}$ mode states, the ν_2^E mode states lack the Coriolis interaction of order ϵ^2. This makes purely vibrational terms in H_{eff} of order ϵ^2 much more prominent. The main rotation-vibration interaction term $H_{ee}^{2(2,E)}$ of order $\epsilon^4 q^2 J^2$ becomes dominant only when $J > N_e \epsilon^{-1} \approx 40 N_e$ (see Tabs. 4 and 9). The structure of the energy level spectrum in the large J limit is further defined by terms of order ϵ^6.

5.3.1 The ν_2^{E} fundamental state

The E-mode fundamental is a "dark" state in the absorption spectrum of P_4. Transitions to this state from the ground state are described by the ϵ^2 term of the transformed dipole moment (see Tab. 6), and the intensity of such transitions is $\propto \epsilon^4 j^2$ or approximately $10^{-6} j^2$ times smaller than that of the ν_3 band. In real life this means that the $0 \to \nu_2$ band simply cannot be observed in absorption spectroscopy. The ν_2^E mode is Raman active. The spontaneous Raman spectrum by Brassington *et al.* [43] recorded at a relatively low resolution of 0.14 cm^{-1} is insufficient for the rotational analysis. A high-resolution Raman spectrum of the $0 \to \nu_2$ transition has not as yet been observed. Due to the low frequency of the band the CARS technique (with a non-collinear BOXCARS arrangement) should probably be most appropriate.

The structure of the ν_2 state can be easily reconstructed from the RE energies in Table 9 with N_f set to 0. Like in the case of ν_3, we set $N_e = 1$ and neglect quartic anharmonicity V_{eeee} in order to obtain a simpler picture. The resulting energy-momentum diagram in Figure 10 shows the small internal splitting of the ν_2 state of order $\epsilon^4 J^2$. The lower of the two branches of the ν_2 state is well split, while the upper branch crosses over itself. This crossover phenomenon is discussed in [44,45]. The value of J at which it occurs and the branch involved is determined by the values and signs of the three parameters, $t^{2(2,E)}$, $t^{3(3,A_2)}$ and $t^{4(4,A_1)}$. The latter are in turn defined by our model.

5.3.2 The $2\nu_2$ overtone

The $2\nu_2$ state has two vibrational components of symmetries A_1 and E; both components are only Raman active and none has been observed experimentally. Our model predicts that the splitting at $J = 0$ equals $\omega \epsilon^2 N_e^2 \approx 1\ \text{cm}^{-1}$ (see Fig. 11, top) and that the energy of the A_1 component is lower. The $2\nu_2$ state is shown in Figure 11, top, in the process of a transition from the structure dominated by vibrational splitting to that of the rotational limit. One of the most intriguing features of this state is the redistribution of a group or, possibly, a branch of levels between its two components. Analysis of the quantum-classical correspondence in such transitional case requires a separate study. We only remark that quantum correction in Table 11 should be used, and the ν_2 mode polyads with large N_e should be considered. Additional RE and their bifurcations should be looked for in such an analysis. On the other hand, the correspondence with RE becomes obvious when the structure of $2\nu_2$ simplifies in the fast rotation limit where $J \gg 80$. To illustrate this limit using "reasonable" J values we drew energy momentum diagrams with artificially small E–A_1 splitting,

$$\Delta_{J=0} = E_E - E_{A_1} = t_{eeee}^{E} - t_{eeee}^{A_1},$$

in the bottom panel of Figure 11.

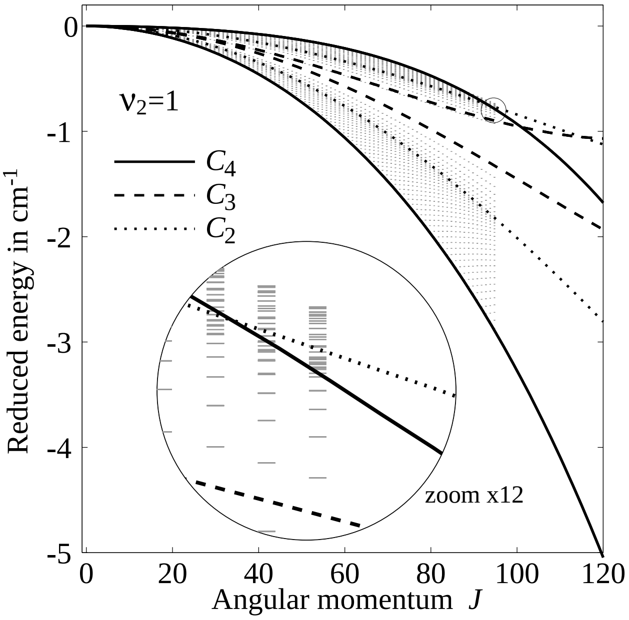

Fig. 10. Relative equilibria of P_4 with $N_e = 1$ and $N_f = 0$, and the structure of the ν_2^E fundamental state. Model prediction.

5.4 The $\nu_2^{\mathsf{E}} + \nu_3^{\mathsf{F}_2}$ state

The $\nu_2^E + \nu_3^{F_2}$ state of P_4 can and probably has been observed experimentally as the upper state of the hot band $\nu_2 \to \nu_2 + \nu_3$. However, no assignment has as yet been given. This makes predictions of the structure of this state particularly interesting. The quantum $\nu_2^E + \nu_3^{F_2}$ state has two vibrational components of symmetries F_1 and F_2. Both components can have Coriolis splitting similar to that of the ν_3 fundamental state (*i.e.*, linear in j). From the RE plot of the $\nu_2^E + \nu_3^{F_2}$ state in Figure 12 we can see that at sufficiently high rotational excitation (when $J > 5$) rotational structure of this state can be regarded as two superimposed systems of three Coriolis-type branches diverging linearly with J. The energies of the C_3 relative equilibria of both systems are very close, while the C_4 equilibria in the upper and lower branch are split. Internal rotational structure of both branches seems to correlate with the initial splittings at $J = 0$. The central branch appears to be more complicated, the process

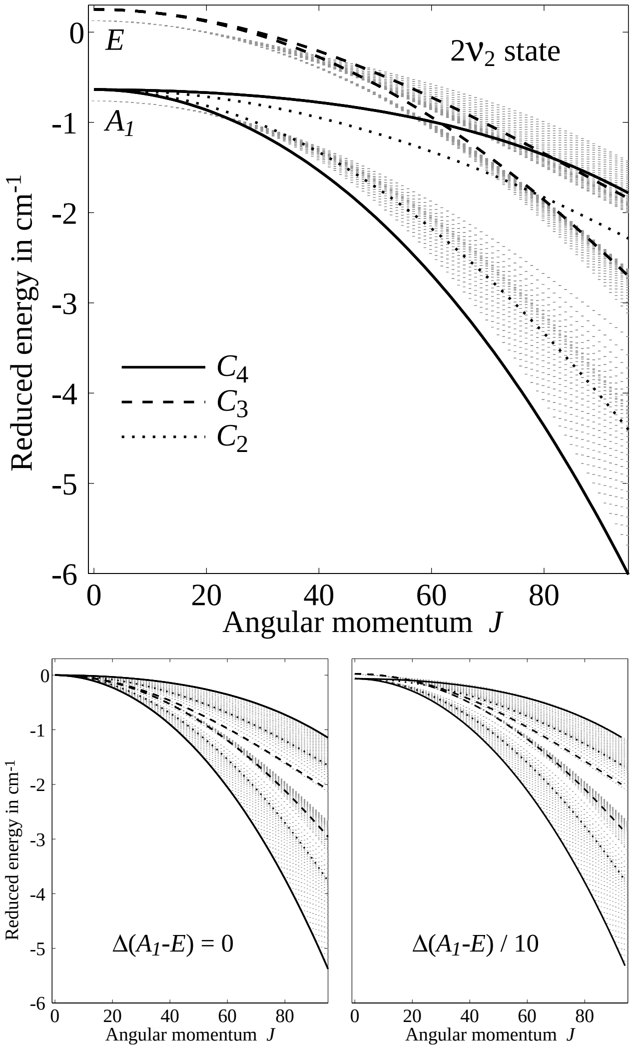

Fig. 11. Relative equilibria of P_4 and the structure of the $2\nu_2$ state calculated for the model Hamiltonian H_{eff} in Table 4. The values $N_e = 2$ and $N_f = 0$ are used for the RE energies. In the bottom panel, the splitting Δ of the two components of $2\nu_2$ is set to zero (left) and taken 10 times smaller (right) than that predicted by the model while all other terms in H_{eff} remain the same.

of transition to the high rotational excitation limit (recoupling) is slower.

The system of vibrational RE at $J = 0$ calls for a special comment. It does not correlate with two quantum states $F_1 \oplus F_2$, instead it represents $n\nu_3 + n\nu_2$ polyads with large n. We can see in Figure 12, bottom, how these polyads change as the value of J rises. The transformation involves additional RE which undergo bifurcations. Analysis of this region, especially at low polyad quantum numbers is always difficult. To circumvent this difficulty in Figures 7 and 10 we purposely disregarded quartic and sextic anharmonic terms of H_{eff}.

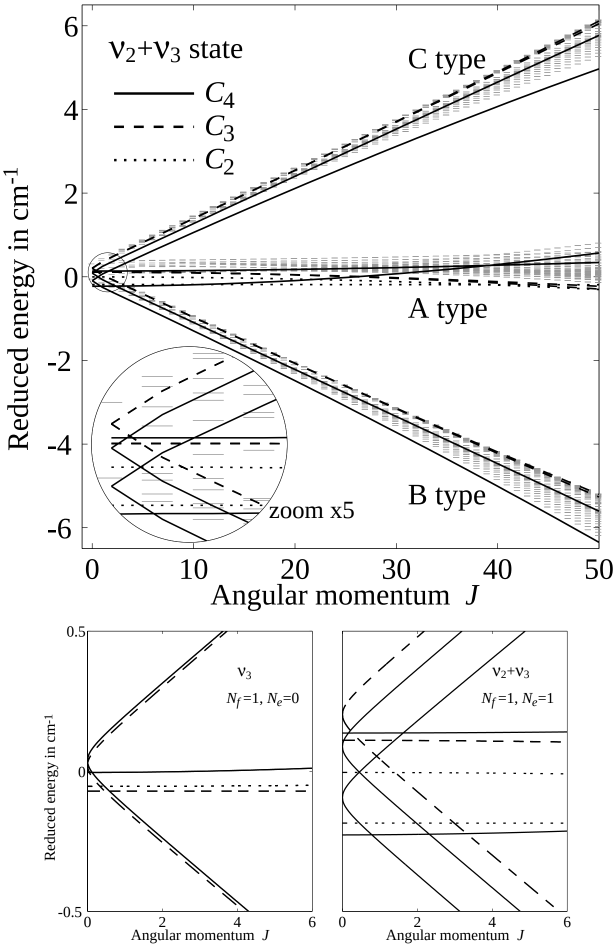

Fig. 12. Energies of relative equilibria of P_4 corresponding to the critical points of the $T_d \times \mathcal{T}$ action on $CP_2 \times CP_1 \times S_2$ and the rotational structure of the $\nu_3^{F_2} + \nu_2^{E}$ state ($N_f = N_e = 1$) predicted on the basis of order 6 normal form. Global view (top), enlarged part of the plot near $J = 0$ (bottom right) and similar plot for the ν_3 state (bottom left).

6 Discussion

The main outcome of this work is a number of interesting qualitative predictions about the structure of rotation-vibration states of the polyatomic molecule P_4. In more general terms, we have presented a complete self-consistent scheme of rotation-vibration analysis based on a classical dynamical study. Rotation-vibration relative equilibria become the primary objective of this analysis, they are studied on the basis of the normalization (averaging) of approximate oscillator symmetries (or symmetries of the polyad approximation) introduced for the vibrational degrees of freedom. Given the complexity of our example, the relative simplicity of the analysis, and the results, we conclude that the proposed method is by far the most adequate technique of extending rotation-vibration analysis far into the region of excited rotation-vibration states.

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$$R^{4(4,A_{1g})} = -\frac{4\sqrt{2}}{\sqrt{15}}\Omega_4,$$

from where we obtain the usual formula for Watson's constant D_t [46,38,39,47]

$$D_t = -\frac{4\sqrt{2}}{\sqrt{15}}h^{4(4,A_1)}.$$

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40. Note that the corresponding 2-form on this C_2 chart of CP_2 is flat, *i.e.*, has the standard matrix $\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$, only to the first order terms in the power series expansion in (z_1, z_2). This restricts our present analysis to linear stability.
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