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Characterization of vibrational transition modes by use of normal forms

Sergio Abbate[1], Danila Ghisletti[2], Antonio Giorgilli[2], Laure Lespade[3], and Giovanna Longhi[1]

[1] Dipartimento di Chimica, Università della Basilicata, Via Nazario Sauro 85,
I-85100 Potenza, Italy

[2] Dipartimento di Matematica, Università di Milano, Via Saldini 50, I-20133, Milano, Italy

[3] Laboratoire de Spectroscopie Moleculaire et Cristalline, Université de Bordeaux I,
Rue de la Liberation 351, F-33405 Talence Cedex, France

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Summary. In this paper we use the Birkhoff–Gustavson perturbation theory to analyze the vibrational modes of two linearly coupled Morse oscillators in the transition region from normal modes to local modes. Our study is based on: truncation of the Hamiltonian written in normal mode coordinates at the 4th order, transformation to normal form and analytical study; construction and use of the approximate integrals of motion of the exact Hamiltonian according to Birkhoff and Gustavson theory. By comparison with a previous analytical study, we demonstrate that perturbation theory, based either on local or normal modes can be used to accurately describe transition modes.

Key words: Transition modes – Normal forms – Action-angle variables

1 Introduction

In this work we carry out a study started in a previous paper on the classical dynamics of two linearly coupled Morse oscillators [1]. Our model Hamiltonian is:

$$H = \sum_{i=1}^{2} \{(p_i^2/2m) + D_i[1 - \exp[-a_i(l_i - l_{i0})]]^2\} + K(l_1 - l_{10})(l_2 - l_{20}) \qquad (1)$$

Here, l_i and l_{i0} are the instantaneous and equilibrium bond lengths, p_i are their conjugate momenta, and m is the reduced mass for both bonds. The relations between the Morse potential parameters D_i, a_i and the mechanical frequencies ω'_i and anharmonicity constant χ_i (cm^{-1}) are:

$$D_i = (hc\omega_i'^2/4\chi_i)$$

$$a_i = \sqrt{(8\pi^2 mc\chi_i/h)}$$

(where h is the Planck's constant, c the speed of light). The numerical experiments which follow were run, as in the previous paper of this series [1], with $\omega'_1 = \omega'_2 = 3000\,\mathrm{cm}^{-1}$, $\chi_1 = \chi_2 = 60\,\mathrm{cm}^{-1}$, $m = 1$ a.u., and $l_{10} = l_{20} = 1.0$ Å.

Systems of this sort have been widely studied in the literature [1–3] especially via numerical integration of the classical equations of motion and a classical perturbative treatment based on local modes; the latter approach goes back to Chirikov's analysis of nonlinear dynamical systems [4] and was adapted to this particular Hamiltonian by Jaffé and Brumer [3]. Following both these approaches we suggested the existence of *transition modes*, with features intermediate between those of local and normal modes. We have characterized these modes and evaluated, via numerical integration, the energy range in which they can be found for the system with the parameters referred to above (typical of methylenic stretchings); for a general case of two equivalent oscillators the perturbative approach mentioned above gives the same energy range for transition modes in analytical form.

We intend here to apply the classical perturbation method, known as the Birkhoff–Gustavson normal form, which privileges the normal mode coordinates [5, 6]. We shall compare different kinds of approximations in studying our physical model: on the one hand, we build approximate integrals of motion in the form of power series expansion truncated at some degree n (in our case $n = 32$); on the other hand, we construct the normal form of the Hamiltonian up to order 4, and reduce it to a system with one degree of freedom via a suitable canonical transformation, so that the corresponding phase space curves can easily be drawn. Since we are especially interested in CH_2-groups, we have considered two oscillators which are not very different from each other and with not too strong a coupling (K is a few hundredths of the principal harmonic force constant). This forces us to take into account the $n{:}n$ resonances, which turn out to be responsible for the phenomenon of transition from normal to local modes.

It is also interesting to compare the normal mode approach used here with the local mode one used in our previous work [1] and in Ref. [3]. The correspondence between quantum Hamiltonians on a local mode basis and on a normal mode basis has been already stated by many authors [7–10]. This equivalence has been shown in general using the property of symmetry of two oscillators of equal frequency, namely the SU(2) symmetry algebra [8–10]. The normal mode Hamiltonian of Darling–Dennison type presented in the literature is derived here from Eq. (1) via a classical perturbative treatment, and it is shown to be nothing but the normal form of the Hamiltonian of Eq. (1) truncated at 4th order.

The paper is organized as follows: in Sect. 2 we recall the essentials of the normal form method, and illustrate how to transform our Hamiltonian of Eq. (1), so that the method can be applied. In Sect. 3 we compare the Poincaré Surfaces of Section (PSS) obtained numerically from the exact Hamiltonian with a) the level curves of the approximate integrals of motion and b) the PSS of the truncated Hamiltonian. In Sect. 4 we investigate the transition modes by examining the phase space curves corresponding to the analytical expression of the 4th order Hamiltonian in terms of action-angles variables. We then make further observations on transition modes in Sect. 5 with the help of both normal and local representation. Finally we report in Appendices A and B some technical details on the computation of the normal form, also considering the general case of non-identical oscillators and kinetic coupling.

2 Perturbative method

We recall here the essential points of the procedure of the normal form methods as introduced by Birkhoff [5a–c]. One starts with an Hamiltonian of the form:

$$H(x, y) = H^{(2)}(x, y) + H^{(3)}(x, y) + \cdots \tag{2}$$

where $(x, y) \in \mathbf{R}^{2n}$ are canonically conjugate variables, $H^{(s)}(x, y)$, for $s > 2$ is a homogeneous polynomial of degree s, and $H^{(2)}(x, y)$ has the form:

$$H^{(2)}(x, y) = \sum \tfrac{1}{2}\omega_i'(x_i^2 + y_i^2) \tag{2a}$$

By a near to identity canonical transformation, the Hamiltonian above can be reduced to the so called Birkhoff normal form. Precisely the transformed Hamiltonian has the form (similar to the original one):

$$Z(\bar{x}, \bar{y}) = Z^{(2)}(\bar{x}, \bar{y}) + Z^{(3)}(\bar{x}, \bar{y}) + \cdots$$

and satisfies the additional properties:

$$Z^{(2)} = H^{(2)}, \quad DZ = 0,$$

where $D \cdot = \{H^{(2)}, \cdot\}$ is the Poisson bracket with the unperturbed Hamiltonian $H^{(2)}$.

A standard result on normal forms is the following: assume that the frequencies $\omega'_1, \ldots, \omega'_n$ of the unperturbed system satisfy r independent resonance relations, with $0 \leqslant r < n$, namely that $\underline{m} \cdot \underline{\omega}' = 0$ for r linearly independent integer vectors $\underline{m} \in \mathbf{Z}^n$; then there are $n - r$ independent first integrals of Z which are suitable linear combinations of the new action variables; precisely they have the form:

$$\tilde{\Phi}(\bar{x}, \bar{y}) = \sum \tfrac{1}{2}\alpha_i(\bar{x}_i^2 + \bar{y}_i^2) \tag{3}$$

where $\underline{\alpha} \in \mathbf{R}^n$ has to satisfy $\underline{m} \cdot \underline{\alpha} = 0$ for all $\underline{m} \in \mathbf{Z}^n$ such that $\underline{m} \cdot \underline{\omega}' = 0$. Thus, in the nonresonant case, the system turns out to be formally integrable; as usual, "formally" means here that we neglect the problems related to the convergence of the series. The case $r = 1$ turns out to be integrable, too. In this case, the normal Hamiltonian Z depends, in general, on all the new action variables $\frac{1}{2}(\bar{x}_i^2 + \bar{y}_i^2)$, $i = 1, \ldots, n$ and on one of the new angles; thus Z cannot be expressed as a function of the $n - 1$ first integrals found above. This gives a total of n first integrals independent and in involution, which ensures integrability in view of Liouville's theorem. In particular, the normal form is always (formally) integrable for systems with two degrees of freedom, since there is at most one resonance relation.

Using again the canonical transformation, which can be given an explicit form [6], we can also express the first integrals $\tilde{\Phi}$ of Z in the old variables, thus getting Φ, the first integrals of H, which are power series in x, y starting with the quadratic term $\tilde{\Phi}$. Such a procedure can be carried out in a very efficient way by using the methods based on Lie transform. We actually used the algorithm and the related computer program illustrated in Ref. [6a].

The application to a system of two degrees of freedom, as the one considered here, goes as follows:

i) In the nonresonant case, $r = 0$, one can construct two first integrals for H, which are perturbations of the harmonic actions $I_j = \frac{1}{2}(x_j^2 + y_j^2)$; such first integrals also turn out to be (formal) action variables for the complete Hamiltonian.

ii) In the resonant case there exists only one first integral which is in fact a perturbation of $H^{(2)}$, but is independent of the Hamiltonian.

This theory has been first introduced in the physical chemistry literature by Swimm and Delos [11a], considering Hénon–Heiles-type Hamiltonians. In order to apply these methods to our system we should first give our Hamiltonian of Eq. (1) the form of Eq. (2). This process is well known as diagonalization of the quadratic part of the Hamiltonian and provides us with normal coordinates. The reason we report it briefly here, is to provide the notation for the coordinates used throughout the paper.

After a Taylor expansion of Eq. (1) in $(l_i - l_{i0})$:

- We introduce mass-weighted coordinates $Q_i = \sqrt{m}(l_i - l_{i0})$ and $P_i = (1/\sqrt{m})\,p_i$. In presence of a kinetic coupling $G_{12}p_1p_2$, the kinetic tensor must be diagonalized first and Q_i assume the symmetric and antisymmetric character of normal coordinates (see Appendix A).

- Secondly the potential must be diagonalized, the normal mode basis which diagonalizes $H^{(2)}$ is:

$$\begin{pmatrix} Q_+ \\ Q_- \end{pmatrix} = \begin{pmatrix} \cos\delta & \sin\delta \\ -\sin\delta & \cos\delta \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} \tag{4}$$

with $\sin 2\delta = 2(K/m)/\sqrt{(\omega_1'^2 - \omega_2'^2)^2 + 4(K/m)^2}$

$$\omega_\pm^2 = \tfrac{1}{2}\{(\omega_1'^2 + \omega_2'^2) \pm \sqrt{(\omega_1'^2 - \omega_2'^2)^2 + 4(K/m)^2}\} \tag{4a}$$

subscripts + and − just refer to the high and low frequency respectively. In the presence of kinetic coupling, Eqs. (4) and (4a) are modified (see Appendix A), but formally all following equations remain the same. The normal coordinates Q_+ and Q_- have symmetric and antisymmetric character respectively if $K > 0$, antisymmetric and symmetric if $K < 0$.

- In frequency-weighted coordinates $x_\pm = \sqrt{\omega_\pm}Q_\pm$, $y_\pm = (1/\sqrt{\omega_\pm})\cdot P_\pm$ we obtain Eqs. (2, 2a); the Hamiltonian $H(x_\pm, y_\pm)$ coincides with one used by Mills and Robiette in their quantum perturbative treatment, with the inclusion of Darling–Dennison coupling [7]. In Appendix B we report $H^{(3)}$ and $H^{(4)}$ for the general case of two different oscillators.

In constructing the Hamiltonian Z, we note that the third-order term $Z^{(3)}$ here vanishes, because we do not consider the 2:1 resonance [12, 13]. The first non-vanishing term is $Z^{(4)}$, which contains quadratic terms in the action variables, and resonant terms, due to the 1:1 resonance, depending on the difference, $\phi_+ - \phi_-$ say, of the phases. We take into account this resonance because in our system we have $\omega_+ \approx \omega_-$. The explicit expression of $Z^{(4)}$ will be given in Sect. 4.

Furthermore, it is evident that the integral associated to our resonance is, from Eq. (3):

$$\tilde{\Phi} = \tfrac{1}{2}(\bar{x}_+^2 + \bar{y}_+^2) + \tfrac{1}{2}(\bar{x}_-^2 + \bar{y}_-^2) = I_+ + I_- = J$$

where I_+ and I_- are the actions of the normal coordinates Q_+ and Q_-. Thus the first integral of our normal Hamiltonian Z is the total action J of the two normal oscillators.

3 Poincaré surfaces of section and level curves

The use of formal expansions as a tool for integration is a common procedure in astronomy. Numerical application to models of the type considered here have been started in the sixties by Contopoulos [5b] and Gustavson [5c]. More recently formal integrals have been used, also in the field of physical chemistry, by many authors [11, 14] in order to calculate energy level distributions. Our purpose here is to compare the detailed structure of phase space obtained from formal integrals with that found by numerical integration, for the case of two Morse oscillators, at low energy. We have treated only the case of identical oscillators. We have integrated numerically the exact Hamiltonian of Eq. (1), expressed in normal coordinates Q_+, Q_- Eq. (4), by an algorithm based on the central point approximation. In Figs. 1A, 2A we report the PSS for two cases of interest for studying the transition normal-local modes (see captions). The same cases have been treated in Ref. [1] with a different representation. Here we use the section plane $Q_+ = 0$, $P_+ \geqslant 0$ (considering cases with $K < 0$) because the limit curve $Q_+ = P_+ = 0$ is a system trajectory, precisely the one representing the pure symmetric motion; this fact, also pointed out a long time ago by Thiele and Wilson [15], guarantees, for the uniqueness of the solutions of the differential Hamilton equations, that no trajectory crosses the limit curve and so no trajectory is partly cancelled by the section.

These PSS are symmetric with respect to the line $P_- = 0$ and the distinction between normal and local modes is evident. As already noted by Lawton and Child [16], each normal mode trajectory is symmetric; both symmetric and the antisymmetric normal mode trajectories are part of the same family of curves. Local modes appear instead as pairs of twin trajectories one lying in the $P_- > 0$ and the other in the $P_- < 0$ semiplane; such trajectories are obtained by choosing initial data with opposite ΔE_{in} (the initial energy difference between the two oscillators). Transition modes are actually part of the latter family. The real distinction between transition and local modes comes from energy and phase considerations on the local basis [1] or on the normal basis oscillators (see next paragraph and Ref. [17]).

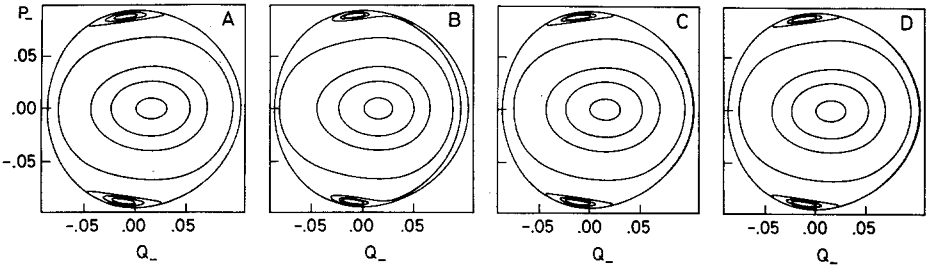


Fig. 1. Poincaré Surfaces of Section in (Q_-, P_-) coordinates for Hamiltonian of Eq. (1) ($K = -0.1$ mdyne/Å, $\omega' = 3000\ \text{cm}^{-1}$, $\chi = 60\ \text{cm}^{-1}$) at total energy $E_T = 2000\ \text{cm}^{-1}$. **A)** Numerically calculated PSS, with initial conditions $\Delta E_{\text{in}} = 0$, 500, 1000, 1500 cm^{-1} and A for the innermost circles; and ± 1500, ± 1000, ± 500 cm^{-1} and S for the couples of curves close to the border. (A means that at time $t = 0$ the local coordinates are $l_1 = l_2 = l_0$ and the sign of p_1 is opposite to that of p_2; S means that $l_1 = l_2 = l_0$ and the sign of p_1 is the same as that of p_2). **B, C, D)** Level curves obtained by use of the approximate integrals of motions at 4th, 8th, and 32nd order, with initial conditions chosen on curves of square A) as described in the text

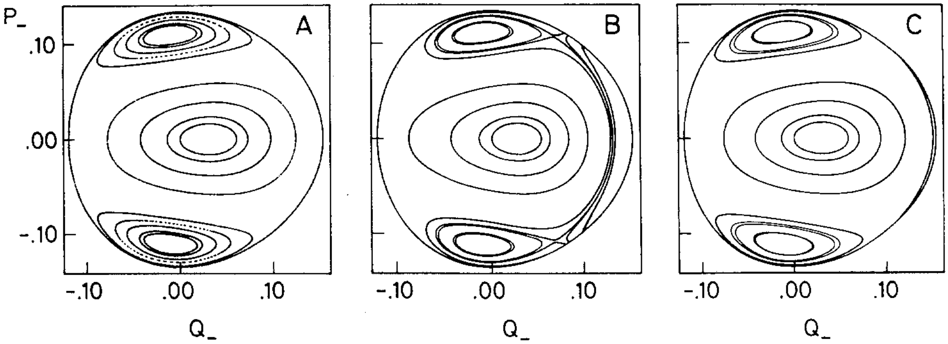


Fig. 2. PSS in (Q_-, P_-) coordinates for Hamiltonian of Eq. (1) $(K = -0.1\,\mathrm{mdyne/Å}$, $\omega' = 3000\,\mathrm{cm}^{-1}$, $\chi = 60\,\mathrm{cm}^{-1})$ at total energy $E_\mathrm{T} = 4000\,\mathrm{cm}^{-1}$. A) Numerically calculated PSS, with initial conditions $\Delta E_\mathrm{in} = 0$, 1000, 2000, 3000 cm^{-1} and A for the innermost circles; and ± 1000, ± 2000, ± 4000, ± 3000, ± 3950 and S for the couples of curves close to the border. **B, C, D)** Level curves obtained by use of the approximate integrals of motions at 4th, 8th, and 32nd order, with initial conditions chosen on curves of square A) as described in the text.

Here, we determine the thresholds, E_tr and E_loc say, at which transition and local modes respectively start to appear by the following criterion, inspired by our previous work [1]. We increase E_T starting from 0, and determine E_tr as the value at which the first nonsymmetric trajectory appears; this actually corresponds to a bifurcation of the central periodic trajectory, giving rise to transition modes in our language. The second threshold E_loc is referred to the character of the particular family of trajectories with $\Delta E_\mathrm{in} = \pm E_\mathrm{T}$. For $E_\mathrm{T} < E_\mathrm{loc}$ the curves in the PSS generated by such trajectories are symmetric, while they become nonsymmetric for $E_\mathrm{T} > E_\mathrm{loc}$. For $E_\mathrm{T} > E_\mathrm{loc}$, transition modes still exist, they give PSS curves inside the $\Delta E_\mathrm{in} = \pm E_\mathrm{T}$ ones, local modes instead are outside such curves.

To compare the PSS with the level curves we report in Figs. 1B, 1C, 1D, 2B, 2C, the same cases in Hamiltonian and total energy treated in Figs. 1A and 2A; these curves are obtained by the formal expansion illustrated above, truncated at 4th, 8th, 32nd order, respectively. The comparison is to be performed by superposition curve by curve. The level curves are found as follows. Denoting by $\Phi(Q_\pm, P_\pm)$ the truncated first integral of H, we determine its value $\Phi(Q^0_\pm, P^0_\pm)$ at an initial point picked up from the PSS curves of Figs. 1A and 2A. Next, we set $Q_+ = 0$, and for Q_-, P_- inside the limiting curve we determine $P_+ \geq 0$ from $H(Q_\pm, P_\pm) = E_\mathrm{T}$, namely the conservation of energy. This makes $\Phi(Q_\pm, P_\pm)$ to actually depend on Q_-, P_- only, and we draw the level lines of this function of two variables. Looking at the Figures, one immediately sees that an 8th order approximation is very good at these low energies: it is much better than the 4th order one, and adding further orders does not actually improve the results, as one sees from comparison of Figs. 1C and 1D. It can be noticed that level curves constructed with these truncated formal integrals introduce spurious new families of curves and false fixed points (see Figs. 1B, 2B) which are partly corrected at higher orders of approximation (Figs. 1C, 1D, 2C) if the total energy is not too high. All the level curves not involved in these artifacts superimpose almost exactly to the PSS curves. From this fact, one can infer that integration via expansions at 8th order describe satisfactorily the dynamics of our system, at the energy of interest for the transition normal modes–local modes.

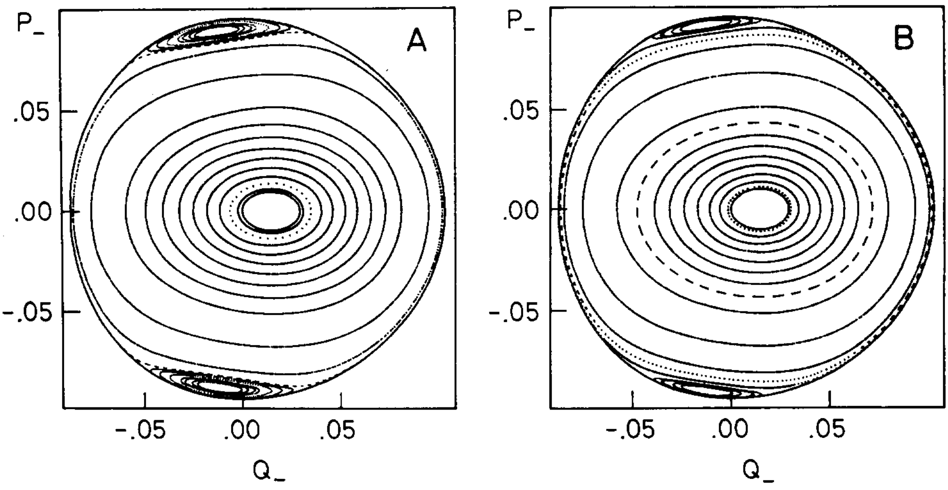


Fig. 3. Comparison of the PSS calculated numerically on the Hamiltonian of Eq. (1) (square *A*) and on its Taylor expansion up to the 4th order (B1) (square *B*): $\omega' = 3000\,\mathrm{cm}^{-1}$, $\chi = 60\,\mathrm{cm}^{-1}$, $K = -0.1$ mdyne/Å, $E_T = 2000\,\mathrm{cm}^{-1}$. The other initial conditions (in terms of ΔE_{in}) are the same in the two cases

Table 1. Comparison of the energy thresholds (in cm^{-1}) of transition mode E_{tr} and of local modes E_{loc} (see text) calculated numerically on the exact Hamiltonian of Eq. (1) (exact), on an Hamiltonian which is a truncation of Eq. (1) at 4th order, at 5th order, at 6th order, and thresholds deduced by the analytical approach of Sect. 4 (analytical)

	exact	4th	5th	6th	analyt.
($K = -0.1$ mdyne/Å)					
E_{tr}	1467.5	1608.5	1481	1493.5	1462
E_{loc}	2902.5	3491.5	2841.5	2907.5	2925
($K = +0.1$ mdyne/Å)					
E_{tr}	1345	1425	1332.5	1342.5	1336.5
E_{loc}	2645.5	3058	2601.0	2649.0	2671.9

A further comparison can be made with PSS obtained from numerical integration of the Hamiltonian truncated at 4th order, as expressed by Eq. (B1). The qualitative results are very good: the fixed points, and all the families of curves are obtained, without artifacts. However, from Fig. 3 it is evident that the region occupied by transition modes and local modes is less extended in the latter case. The same seems to happen in Figs. 1B, 2B for the level curves with 4th order truncation. Quantitatively we can test the 4th order approximation of the Hamiltonian by numerically calculating the thresholds E_{tr} and E_{loc}. We report the results in Table 1 as derived from the "exact" and the 4th order Hamiltonian.

4 Phase space in the resonant angle-action variables

To study analytically the dynamics of the system, we examined directly the truncated Hamiltonian $Z(\bar{x}, \bar{y}) = Z^{(2)}(\bar{x}, \bar{y}) + Z^{(4)}(\bar{x}, \bar{y})$, which is built on the assumption of a 1 : 1 resonance due to the physical requirement $\omega_+ \approx \omega_-$. At this point it is useful to introduce the action-angle variables $\phi_\pm$, $I_\pm$ for the normal harmonic oscillators. The expression obtained for $Z^{(4)}$ depends only on one angle coordinate $\theta_R = \phi_+ - \phi_-$, so there must be a cyclic coordinate, say θ. From the definition of θ_R, it turns out that the action canonically associated with θ is $J = I_+ + I_-$, implying that this is a constant of motion, as already found in Sect. 2. Following a standard scheme, we perform the canonical transformation:

$$\begin{aligned} \theta_R &= \phi_+ - \phi_- \qquad & J_R &= I_+ \\ \theta &= \phi_- & J &= I_+ + I_- \end{aligned}$$

The Hamiltonian thus obtained for identical oscillators has the general form:

$$\begin{aligned} Z = Z^{(2)} + Z^{(4)} = BJ_R^2 + (AJ + \Delta)J_R + CJ_R(J - J_R)\cos 2\theta_R \\ + bJ^2 + \omega_- J \end{aligned} \tag{5}$$

with coefficients A, B, C, Δ, b that we give here explicitly. Notice that the term ΔJ_R is due to the condition of nonexact resonance: $\omega_+ \neq \omega_-$. We get the values:

$$\begin{aligned}
B &= a + b - c \\
A &= -2b + c \\
a &= (3/2)K_{++++} - (15/4)K_{+++}^2/\omega_+ + (1/4)K_{++-}^2 \\
&\quad \times (3\omega_-^2 - 8\omega_+^2)/\omega_-(4\omega_+^2 - \omega_-^2) \\
b &= (3/2)K_{----} - (15/4)K_{---}^2/\omega_- + (1/4)K_{+--}^2 \\
&\quad \times (3\omega_+^2 - 8\omega_-^2)/\omega_+(4\omega_-^2 - \omega_+^2) \\
c &= K_{++--} - 3K_{+++}K_{+--}/\omega_+ - 3K_{---}K_{++-}/\omega_- \\
&\quad - 2\omega_+ K_{++-}^2/(4\omega_+^2 - \omega_-^2) - 2\omega_- K_{+--}^2/(4\omega_-^2 - \omega_+^2) \\
C &= K_{++--}/2 + K_{+++}K_{+--}/4\omega_+ + K_{---}K_{++-}/4\omega_- \\
&\quad + 3\omega_+ K_{+--}K_{+++}/4(4\omega_-^2 - \omega_+^2) \\
&\quad + 3\omega_- K_{++-}K_{---}/4(4\omega_+^2 - \omega_-^2) \\
&\quad - K_{++-}^2\omega_+/\omega_-(2\omega_+ - \omega_-) - K_{+--}^2\omega_-/\omega_+(2\omega_- - \omega_+) \\
\Delta &= \omega_+ - \omega_-
\end{aligned}$$

The above constants K's are the coefficients of the Hamiltonian $H(x_\pm, y_\pm)$ as reported in Eq. (B1); in particular, for two identical oscillators the only nonvanishing constants (for symmetry reasons) are:

if $K > 0$, $K_{+++} = -\omega'^2\sqrt{\chi}/2\omega_+^{3/2}$; $K_{+--} = -3\omega'^2\sqrt{\chi}/2\omega_-\omega_+^{1/2}$

if $K < 0$, $K_{---} = \omega'^2\sqrt{\chi}/2\omega_-^{3/2}$; $K_{++-} = 3\omega'^2\sqrt{\chi}/2\omega_+\omega_-^{1/2}$

and $K_{++++} = 7\omega'^2\chi/24\omega_+^2$; $K_{----} = 7\omega'^2\chi/24\omega_-^2$

$K_{++--} = 7\omega'^2\chi/4(\omega_+\omega_-)$ regardless of the sign of K.

We use wavenumber units for energies and frequencies, and J and J_R are dimensionless actions. The frequencies $\omega_\pm$ are obtained from Eq. (4a) with $\sqrt{(K/m)}$ rad/sec = $1301.9\sqrt{(K/m)}$ cm^{-1}. The case of two nonidentical oscillators is discussed in Appendix B.

Equation (5) has the advantage that it can be handled analytically so that information can be gained about the system in general, and not only inferred from the particular numerical experiment chosen. It can be also useful to consider the following approximate expression, obtained by neglecting the terms of the order of $\chi\Delta/\omega'^2$ ($\Delta = K/(4\pi^2c^2m)$):

$$Z = \chi J_R^2 + (\Delta - \chi J)J_R - \chi J_R(J - J_R)\cos 2\theta_R - \tfrac{1}{2}\chi J^2 + \omega_- J$$

If the region of physical interest $0 \leqslant J_R \leqslant J$, there are two fixed points, when:

$$J > -\Delta/(A + C) \approx (\Delta/2\chi), \tag{6}$$

namely:

$$\theta_R = 0 \quad J_R = [(A + C)/2(C - B)]J + \Delta/2(C - B) \approx (J/2) - (\Delta/4\chi) \text{ (center)}$$
$$J_R = 0 \quad \cos 2\theta_R = -(AJ + \Delta)/CJ \approx -1 + (\Delta/\chi J) \text{ (saddle)}$$

The phase space curves $Z(J_R, \theta_R) = E_T$ for the case $K < 0$ and for three different values of J are reported in Fig. 4. Our aim here is to find the range of total action for the different kinds of modes. A similar figure was obtained by Levine et al. [10] by varying anharmonicity and the coupling of the oscillators and keeping the total action fixed.

Due to our definition of J_R, if $K < 0$, the straight line in Fig. 4 at $J_R = J$ corresponds to the antisymmetric normal mode and that at $J_R = 0$ corresponds to the pure symmetric mode (vice versa for $K > 0$). For low values of J only open curves are present, corresponding to normal modes. At $J = -\Delta/(A + C)$ (see Eq. (6)) the centers and the saddles appear on the line $J_R = 0$, and the pure symmetric mode becomes unstable for $K < 0$ (the instability regards the antisymmetric mode if $K > 0$). At higher value of J, closed curves appear around the centers, so normal modes get "phase locked" and combine to generate different kinds of modes, namely transition and local modes. Thus $-\Delta/(A + C)$ can be interpreted as the threshold for transition modes. Due to the $2\theta_R$ dependence of Eq. (5), closed curves show up as pairs around $\theta_R = 0$ and $\theta_R = \pi$, generating modes involving more bond 1 than bond 2 in $\theta_R = 0$ and vice versa in $\theta_R = \pi$ (each single transition and local mode does not respect the symmetry of the two bonds, but they come in degenerate pairs). When closed curves do not cross the line $J_R = J/2$, i.e., they lie in the lower half of phase space, they preserve the phase of the normal mode of lower frequency (the one labelled by $-$, the symmetric one if $K < 0$) so they are transition modes. When the closed curves cross the line $J_R = J/2$, the modes do not preserve the phase of one normal mode anymore, so they can be said to be the local modes (according to the distinction transition/local given in Ref. [1]). One can find that the separatrix between closed and open curves is the curve relative to $E_T = bJ^2 + \omega_- J$, in particular this curve intersects the axis $\theta_R = 0$ at $J_R = 0$ and $J_R = [(A + C)J + \Delta]/(C - B) \approx J - (\Delta/2\chi)$. This means that the threshold for local modes is

$$J = -2\Delta/(2A + C + B) \approx \Delta/\chi \tag{7}$$

With Eqs. (6) and (7) one can obtain expressions for the two thresholds in total energy. When $J = -\Delta/(A + C)$, $E_T = bJ^2 + \omega_- J$ in the center and E_T is greater

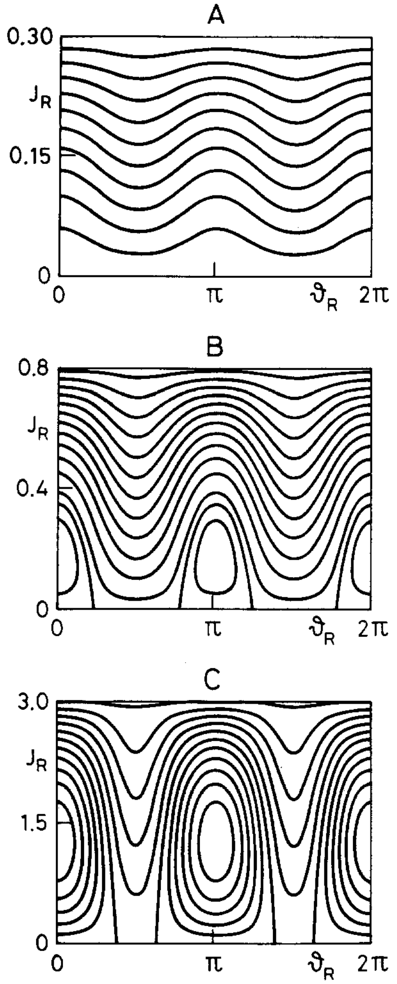


Fig. 4. Phase Space Portrait in resonant action-angle variables $\theta_R = \phi_+ - \phi_-$ and $J_R = I_+$ calculated analytically as presented in Sect. 4. **A**): Total action $J = I_+ + I_- = 0.3$; **B**): $J = 0.8$; **C**): $J = 3.0$ (compare also with the results of Ref. [1] ($\omega' = 3000\,\mathrm{cm}^{-1}$, $\chi = 60\,\mathrm{cm}^{-1}$, $K = -0.1$ mdyne/Å)

for all other phase space curves, thus the minimum total energy E_{tr} at which centers appear (that is E_{tr} as defined in section III) is $E_{\mathrm{tr}} = bJ^2 + \omega_- J \approx -\frac{1}{2}\chi J^2 + \omega_- J$ with J given in Eq. (6). When $J = -2\Delta/(2A + B + C)$, $E_{\mathrm{T}} = bJ^2 + \omega_- J$ on the separatrix which is the first closed curve crossing $J/2$, and E_{T} is greater for all open curves, thus the minimum total energy at which closed curves appear also in the upper half of phase space (that is E_{loc}) is $E_{\mathrm{loc}} = bJ^2 + \omega_- J \approx -\frac{1}{2}\chi J^2 + \omega_- J$ with J given by Eq. (7).

We computed the values of the thresholds with different approximations. The results are reported in Table 1. The values in column 1 are computed by numerically integrating the exact Hamiltonian; in column 2, 3, and 4 we report the values obtained by numerically integrating the Taylor expansion of the Hamiltonian, truncated at orders, 4, 5, and 6, respectively. Finally, in column 5 the same values are estimated by using Eqs. (6) and (7). It is seen that the latter values look pretty good, when compared with the values in column 1. In contrast, the truncation at order 4, namely $H^{(2)} + H^{(3)} + H^{(4)}$, gives too high values, and one has to consider the terms of order 5 in order to get an approximation comparable with that of the normal form $Z^{(2)} + Z^{(4)}$. The addition of terms of order 6 gives just a small correction. Thus, it seems that the normal form already contains information hidden in higher terms of the Taylor expansion. To understand this, one should remark that $Z^{(5)}$ vanishes in our case, so that the normal forms at order 4 and 5 do coincide. Here too, it is reasonable to expect that the addition of the term $Z^{(6)}$ gives just a small correction, so that the approximation of 4th order in the normal form is actually enough to obtain a good qualitative and quantitative description of the dynamics.

It is also interesting to compare these values with the thresholds obtained from another perturbative treatment basėd on nonlinear reasonances between two Morse oscillators. The latter are reported in our previous work [1] for transition modes and in the work by Jaffé and Brumer [2] for local modes. In the limit of weak coupling, one obtains the same values $\Delta/2\chi$ and Δ/χ respectively, but referred to a total action J which is the sum of the actions of the two uncoupled Morse oscillators. The total energy thresholds are given there by the approximate expression:

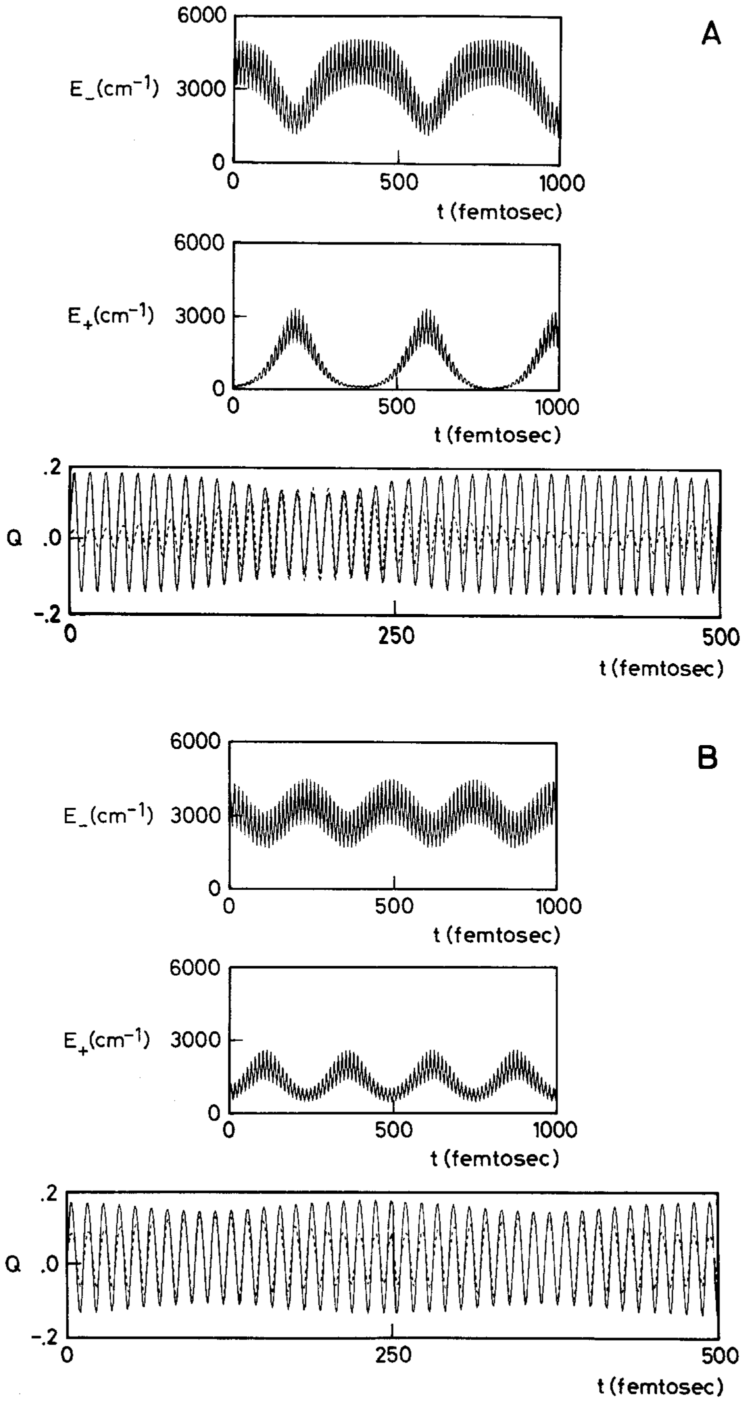
$$E_{\mathrm{T}} \approx \omega' J - \tfrac{1}{2}\chi J^2 - (|K|/4\pi^2 mc^2)\tfrac{1}{2}J = \omega_- J - \tfrac{1}{2}\chi J^2$$

which formally coincides with the expression derived above. This correspondence reflects the equivalence of the representations of the Hamiltonian in local and normal modes, obtained by SU(2) transformation [8, 9]. The existence of two separate thresholds just illustrated is in good agreement with the work by Shirts [18], who found the change in stability of the pure symmetric mode (in the case $K < 0$) at lower energy than the threshold of local modes, which was defined previously by Jaffé and Brumer [2] as the energy at which "the resonance width is less than the total range of action".

5 Comparison with previous results

The assignment of normal mode character or local mode character to the curves in the (θ_R, J_R) representations of Fig. 4 is in agreement with the work by Kellman [8], which illustrates quite well how the phase space curves in resonant action-angle variables are a projection of the curves of a sphere in the phase space onto a plane. In the normal mode representation; the fixed points corresponding to pure normal modes are chosen as poles of the sphere and, when projected, become the limiting open curves. The other fixed points on the sphere, generated by the normal mode resonance, are located symmetrically at right angles with respect to the normal modes fixed points only in the limit $\Delta/\chi \to 0$, and only in this case correspond to pure local modes. In the case of finite Δ/χ they are symmetrically disposed with respect to the pure symmetric normal mode (when $K < 0$) at an angle lower than 90°. In this situation there are curves around these fixed points for which a phase relation persists between the two pure local mode components, and between the two pure normal mode components; besides, the relative action J_R of the two components never changes sign so that the energy is not totally exchanged. These kinds of curves on the phase space sphere correspond to transition modes according to our previous classification.

In this spirit we have confirmed our description of the (J_R, θ_R) representation of the previous section through plots obtained by numerical integration and reported in Fig. 5. We give the time dependence of the pure symmetric and antisymmetric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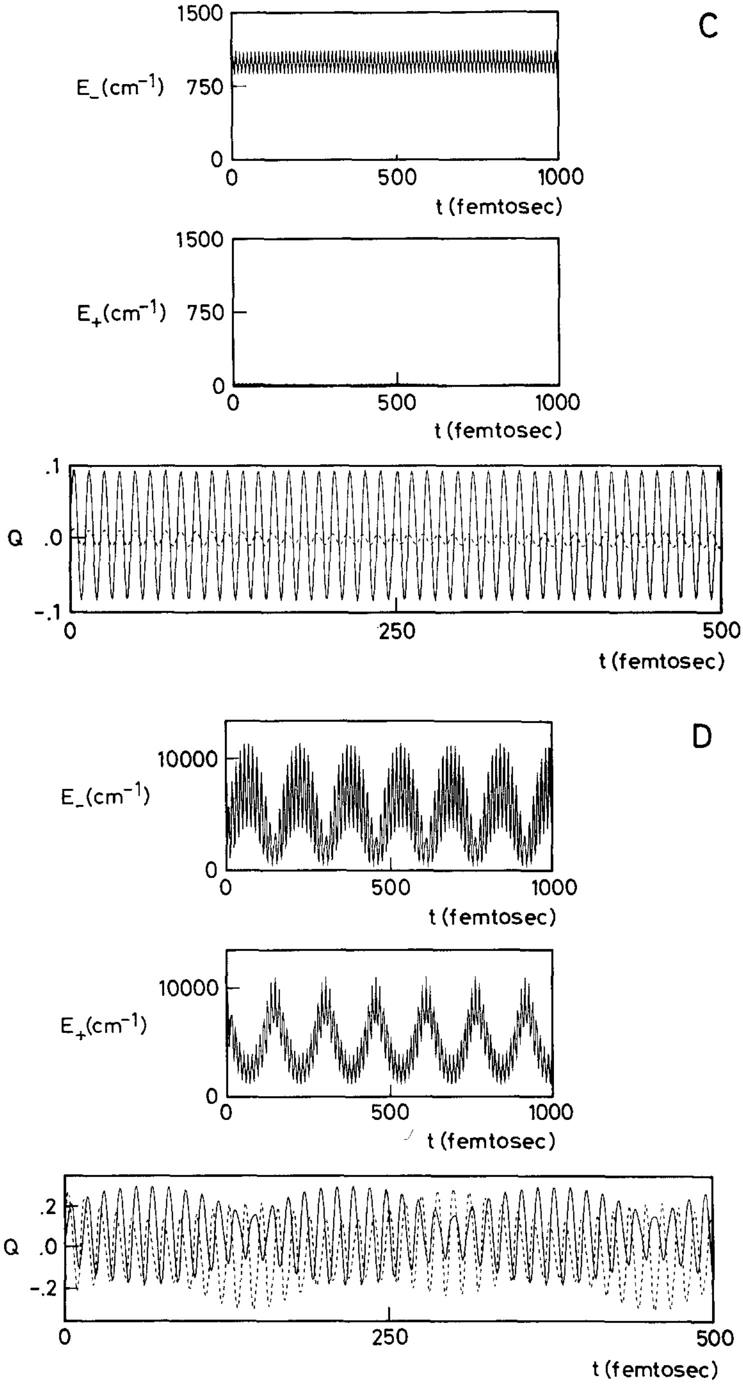

Fig. 5. Time dependence (in femtosec) of energies E_+, E_- (in cm^{-1}) of Eq. (12) and of oscillators amplitudes Q_+ and Q_- (in Å) for the antisymmetric and symmetric normal coordinates (in the latter case Q_+ is drawn *solid* and Q_- *dashed*) for local modes (square *A*, $E_T = 4000\,\text{cm}^{-1}$) and transition modes (square *B*, $E_T = 4000\,\text{cm}^{-1}$) and normal modes (squares *C*, $E_T = 1000\,\text{cm}^{-1}$ and *D*, $E_T = 9000\,\text{cm}^{-1}$)

coordinates Q_+, Q_- and of their approximate energy contributions E_+ and E_-. The symmetric and antisymmetric energies $E_\pm$ reported in Fig. 5 are defined in quadratic approximation as:

$$E_\pm = \tfrac{1}{2}\omega_\pm(x_\pm^2 + y_\pm^2) \tag{8}$$

These plots confirm that:

– In the normal mode regime the symmetric and antisymmetric coordinates have no phase relation (Figs. 5C, 5D), while in the transition and local mode regimes they present "phase locking" (Figs. 5A, 5B);

– In the transition mode regime one normal oscillator is always predominant (Fig. 5B), namely it has always higher energy than the other, as opposite to what happens for local modes (Fig. 5A).

– In the normal mode regime the energy exchange can be of either type as shown in Figs. 5C, 5D; this is related to what was found in Fig. 4, where open curves may or may not cross the line $J_R = J/2$. In any case the exchange between the two energies is never total as observed in the case of local mode basis representation: indeed local mode basis respects the symmetry of the problem, while symmetric and antisymmetric modes are not equivalent.

6 Conclusions

In this work we reexamined a system of two coupled anharmonic oscillators and characterized, from the point of view of normal coordinates, the vibrational modes at the transition between the normal mode and the local mode regimes. In doing this, we compared different perturbative treatments and different degrees of approximation. First of all we considered at which degree of approximation the Birkhoff–Gustavson perturbation treatment yields accurate results at low total energy:

i) We compared level curves obtained from formal expansion of an integral of motion with numerically obtained PSS; we found that a satisfactory match is obtained with an 8th order truncation but not at lower orders. By the way, this test, performed in the periodic regime, is a necessary premise to eventually applying it for a semiclassical quantization of the system at higher energies, as already done for example for the Hénon–Heiles Hamiltonian.

ii) We compared the values of the thresholds of local and transition modes obtained in three different ways, namely integration of the exact Hamiltonian, integration of the Taylor expansion of the Hamiltonian truncated at different orders, and analysis of the Birkhoff normal form at order 4. We conclude that in this respect the fourth order of the normal form already gives good results, which are comparable with a higher degree expansion of the Hamiltonian.

Finally we have demonstrated that the 4th order normal form perturbation theory based on normal modes can be used to describe transition modes as accurately as the perturbation theory based on local modes. We found that in normal coordinates, Q_+ and Q_- transition modes show no energy interchange, but Q_+ and Q_- are phase locked as in local mode coordinates. The classification of modes derived from the plots of energies and phases allows us to classify the curves in the phase space of the resonant angle-action variables of the perturbative treatment (resonance between normal modes). This permits a one to one correspondence with curves of the phase space of the resonance between local modes. At the zeroth order in $\chi\Delta/\omega'^2$ we found the same thresholds in J in the two perturbative treatments, where J is the sum of the actions of the two harmonic oscillators in one case, and of the actions of the two Morse oscillators in the other case.

Appendix A

We consider two Morse oscillators (two methylenic CHs for example) coupled both kinetically and potentially as follows:

$$H=\sum p_i^2/2m+G_{12}p_1p_2+\sum D_i[1-\exp[-a_i(l_i-l_{i0})]]^2+K(l_1-l_{10})(l_2-l_{20})$$

Normal coordinates are those which diagonalize the whole linearized Hamiltonian, characterized by a kinetic matrix and a force constant matrix of the kind:

$$\mathbf{G}=\begin{pmatrix} m^{-1} & G_{12} \\ G_{12} & m^{-1} \end{pmatrix} \quad \text{and} \quad \mathbf{F}_1=\begin{pmatrix} \omega_1'^2 m & K \\ K & \omega_2'^2 m \end{pmatrix}$$

such that the Hamiltonian can be put in the form:

$$H=\tfrac{1}{2}\tilde{\mathbf{p}}\mathbf{G}\mathbf{p}+\widetilde{(\mathbf{l}-\mathbf{l}_0)}\mathbf{F}(\mathbf{l}-\mathbf{l}_0)$$

(~ means here transposed).

The coordinates Q_1 and Q_2 which diagonalize the kinetic tensor and reduce it to the identity are given by [19]:

$$(\mathbf{l}-\mathbf{l}_0)=\mathbf{D}\mathbf{Q}; \qquad \mathbf{P}=\tilde{\mathbf{D}}\mathbf{p}$$

with $\mathbf{D}=\mathbf{A}\Lambda^{1/2}$ where $\mathbf{G}\mathbf{A}=\mathbf{A}\Lambda$
So:

$$\mathbf{Q}=\mathbf{D}^{-1}(\mathbf{l}-\mathbf{l}_0)=\begin{pmatrix} -[2(1/m-G_{12})]^{-1/2} & [2(1/m-G_{12})]^{-1/2} \\ -[2(1/m+G_{12})]^{-1/2} & -[2(1/m+G_{12})]^{-1/2} \end{pmatrix}\begin{pmatrix} l_1-l_{10} \\ l_2-l_{20} \end{pmatrix} \tag{A1}$$

$$H=\tfrac{1}{2}\tilde{\mathbf{P}}\mathbf{P}+\tilde{\mathbf{Q}}\mathbf{F}_Q\mathbf{Q} \qquad \mathbf{F}_Q=\tilde{\mathbf{D}}\mathbf{F}_1\mathbf{D}$$

Diagonalization of the potential term $\mathbf{F}_Q$ gives:

$$\omega_\pm^2=\tfrac{1}{2}(\omega_1'^2+\omega_2'^2)+KG_{12}\pm\tfrac{1}{2}\{(\omega_1'^2\underset{2}{-}\omega_2'^2)^2+4K^2/m^2+m^2G_{12}^2[(\omega_1'^2+\omega_2'^2)$$

$$-(\omega_1'^2-\omega_2'^2)^2]+4KG_{12}(\omega_1'^2+\omega_2'^2)\}^{1/2} \tag{A2}$$

with a normal mode basis Q_+, Q_- given by Eq. (7) with:

$$\cos 2\delta=\frac{-[K/m+\frac{1}{2}mG_{12}(\omega_1'^2+\omega_2'^2)]}{\frac{1}{2}\{(\omega_1'^2-\omega_2'^2)^2+4K^2/m^2+m^2G_{12}^2[(\omega_1'^2+\omega_2'^2)^2-(\omega_1'^2-\omega_2'^2)^2]+4KG_{12}(\omega_1'^2+\omega_2'^2)\}^{1/2}} \tag{A3}$$

For identical oscillators ($\omega'_1 = \omega'_2$):

$$\omega_{\pm}^2 = \omega'^2 + KG_{12} \pm |K/m + mG_{12}\omega'^2|$$

$$\cos 2\delta = -\operatorname{sgn}(K/m + mG_{12}\omega'^2)$$

So when $K \geqslant -G_{12}\omega'^2 m^2$: $\begin{cases} Q_+ = Q_2 \\ Q_- = -Q_1 \end{cases}$

the mode at higher frequency is symmetric, the one at lower frequency antisymmetric. On the opposite, when $K \leqslant -G_{12}\omega'^2 m^2$:

$$\begin{cases} Q_+ = Q_1 \\ Q_- = Q_2 \end{cases}$$

the mode at higher frequency is antisymmetric, the one at lower frequency symmetric.

As already stated in Ref. [1], in presence of a kinetic coupling the system behaves as if the effective coupling constant were:

$$K_{\text{eff}}/m = K/m + mG_{12}\omega'^2.$$

Appendix B

The Birkhoff–Gustavson normal form for two different Morse oscillators of mechanical frequencies ω'_1 and ω'_2 and anharmonicities χ_1 and χ_2, respectively, which are coupled through a linear term in the potential, is given by:

$$H^{(2)}/hc = \tfrac{1}{2}[\omega_+(x_+^2 + y_+^2) + \omega_-(x_-^2 + y_-^2)] \tag{B1}$$

$$H^{(3)}/hc = K_{+++}x_+^3 + K_{---}x_-^3 + K_{++-}x_+^2 x_- + K_{+--}x_+ x_-^2$$

$$\begin{aligned} H^{(4)}/hc = {} & K_{++++}x_+^4 + K_{----}x_-^4 + K_{++--}x_+^2 x_-^2 \\ & + K_{+++-}x_+^3 x_- + K_{+---}x_+ x_-^3 \end{aligned}$$

where:

$$\begin{aligned}
K_{+++} &= (-\omega_1'^2\sqrt{\chi_1}\cos^3\delta - \omega_2'^2\sqrt{\chi_2}\sin^3\delta)/(\sqrt{2}\omega_+^{3/2}) \\
K_{---} &= (+\omega_1'^2\sqrt{\chi_1}\sin^3\delta - \omega_2'^2\sqrt{\chi_2}\cos^3\delta)/(\sqrt{2}\omega_-^{3/2}) \\
K_{++-} &= (+\omega_1'^2\sqrt{\chi_1}\cos\delta - \omega_2'^2\sqrt{\chi_2}\sin\delta)\,3\cos\delta\sin\delta/(\sqrt{2}\omega_+\omega_-^{1/2}) \\
K_{+--} &= (-\omega_1'^2\sqrt{\chi_1}\sin\delta - \omega_2'^2\sqrt{\chi_2}\cos\delta)\,3\cos\delta\sin\delta/(\sqrt{2}\omega_-\omega_+^{1/2}) \\
K_{++++} &= (\omega_1'^2\chi_1\cos^4\delta + \omega_2'^2\chi_2\sin^4\delta)(7/12\omega_+^2) \\
K_{----} &= (\omega_1'^2\chi_1\sin^4\delta + \omega_2'^2\chi_2\cos^4\delta)(7/12\omega_-^2) \\
K_{++--} &= 7\sin^2\delta\cos^2\delta(\omega_1'^2\chi_1 + \omega_2'^2\chi_2)/(2\omega_+\omega_-) \\
K_{+++-} &= 7\cos\delta\sin\delta(-\omega_1'^2\chi_1\cos^2\delta + \omega_2'^2\chi_2\sin^2\delta)/(3\omega_+^{3/2}\omega_-^{1/2}) \\
K_{+++-} &= 7\cos\delta\sin\delta(-\omega_1'^2\chi_1\cos^2\delta + \omega_2'^2\chi_2\sin^2\delta)/(3\omega_+^{3/2}\omega_-^{1/2})
\end{aligned}$$

The terms of the expansion of the Hamiltonian and all higher order force constants are in wavenumber units, with dimensionless coordinates $x_\pm$, $y_\pm$. $\omega_\pm$ are given by Eq. (4a) in the text. $\cos\delta$ and $\sin\delta$ are obtained from Eq. (4) in the text. When the two oscillators are equivalent, some constants identically vanish for symmetry reasons, in particular H will contain only even powers of the antisymmetric coordinate, which is x_+ or x_- depending on the sign of K: indeed $\delta = \pi/4$ for $K > 0$ and $\delta = 3\pi/4$ for $K < 0$. It can be checked that the Hamiltonian in Eq. (B1), with the definition of the anharmonic force constants that follow, coincides with the Darling–Dennison Hamiltonian considered by Mills and Robiette [6].

Introducing angle-action variables and the resonant angle $\theta_R = \phi_+ - \phi_-$ as described in the text, the Hamiltonian Z in normal form at fourth order is given by Eq. (5) in the text with the addition of the following term: (see also Ref. [9b])

$$(DJ_R + EJ)\sqrt{J_R(J - J_R)}\cos\theta_R \tag{B2}$$

where:

$$\begin{aligned}
D = 2(d - e) = {} & (3/2)K_{+++-} - (3/2)K_{+---} - (5/2)K_{+++}K_{++-}/\omega_+ \\
& + (5/2)K_{---}K_{+--}/\omega_- \\
& - (3/2)[(3\omega_- + 2\omega_+)\omega_+/(4\omega_+^2 - \omega_-^2)\omega_-]K_{+++}K_{++-} \\
& + (3/2)[(3\omega_+ + 2\omega_-)\omega_-/(4\omega_-^2 - \omega_+^2)\omega_+]K_{---}K_{+--} \\
& - (3/2)[(3\omega_- + 2\omega_+)\omega_+/(4\omega_+^2 - \omega_-^2)\omega_-]K_{+++}K_{++-} \\
& + (3/2)[(3\omega_+ + 2\omega_-)\omega_-/(4\omega_-^2 - \omega_+^2)\omega_+]K_{---}K_{+--} \\
& - (1/2)[(3\omega_+ + 2\omega_-)\omega_-/(4\omega_-^2 - \omega_+^2)\omega_+]K_{++-}^2 \\
& + (1/2)[(3\omega_- + 2\omega_+)\omega_+/(4\omega_+^2 - \omega_-^2)\omega_-]K_{+--}^2
\end{aligned}$$

$$\begin{aligned}
E = 2e = {} & (3/2)K_{---+} - (5/2)K_{---}K_{--+}/\omega_- \\
& - (3/2)[(3\omega_+ + 2\omega_-)\omega_-/(4\omega_-^2 - \omega_+^2)\omega_+]K_{---}K_{--+} \\
& - (1/2)[\omega_+(3\omega_- + 2\omega_+)/\omega_-(4\omega_+^2 - \omega_-^2)]K_{--+}K_{-++} \\
& - [(8\omega_-^2 - 3\omega_+^2)/4\omega_+(4\omega_-^2 - \omega_+^2)]K_{--+}K_{-++}
\end{aligned}$$

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