Gustavson's procedure and the dynamics of highly excited vibrational states

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The well-known Birkhoff–Gustavson canonical perturbation theory has been used so far to obtain a reasonable approximation of model systems near the bottom of the well. It is argued in the present work that Gustavson's calculation procedure is also a powerful tool for the study of the dynamics of highly excited vibrational states, as soon as the requirement that the transformed Hamiltonians be in Birkhoff's normal form is dropped. Mathematically, this amounts to modifying the content of Gustavson's null space. Physically, the transformed Hamiltonians are of the single or multiresonance type instead of just trivial Dunham expansions, even though no exact resonance condition is fulfilled. This idea is checked against 361 recently calculated levels of HCP up to 22 000 cm^{-1} above the bottom of the well and involving up to 30 quanta in the bending degree of freedom. Convergence up to 13th order of perturbation theory and an average absolute error as low as 2.2 cm^{-1} are reported for a two-resonance Hamiltonian, whereas the Dunham expansion converges only up to 4th order at an average error of 215 cm^{-1}. The principal advantages of the resonance Hamiltonians compared to the exact one rely on its remaining good quantum numbers and classical action integrals. Discussions of the limitations of the method and of the connections to other canonical perturbation theories, like Van Vleck or Lie transforms, are also presented. [S0021-9606(98)01730-9]

I. INTRODUCTION

The experimentalist's first step for deriving information from vibrational spectra usually consists of developing a simple Hamiltonian, which is able to reproduce the measured spectrum. Examples for such Hamiltonians are the Dunham expansion[1–4] and the single resonance Hamiltonian used to model molecules with Fermi or Darling–Dennison resonances.[5–12] Obviously, the broader the energy range encompassed by the spectrum, the more terms are needed in the Hamiltonian to take into account those effects, the strength of which increase with energy, like diagonal anharmonicities and off-diagonal couplings between zero order modes. Gradually, the fit of these terms to the observed transition frequencies becomes more and more tedious. This is due in part to their very rapidly increasing number, but most of all to the very strong correlations which exist among them and cause the problem to become numerically unstable.

Accordingly, the problem must be approached from a completely different viewpoint at sufficiently high energies. That is, one must first compute an accurate potential energy surface (PES) and then solve exactly the multidimensional Schrödinger equation. Though still limited to small molecules, principally triatomic ones and a few tetratomics, significant advances have been registered in this field in the last few years.[13–16] In addition to the difficulties inherent to quantum mechanical variational calculations, the principal drawback of this approach lies in the working of the results coming out from the computer codes. Indeed, essentially all the zero order levels are coupled for highly excited molecules studied along these lines, and even the very basic information, like the assignment to sets of approximate good quantum numbers, requires the visual inspection of several hundred or even thousands of quantum wave functions. This is both time and patience consuming. Similarly, from the classical point of view, problems as fundamental as the search for periodic orbits require complex numerical methods like multiple shooting algorithms or damped and quasi-Newton iterative methods[17]—not to speak of action integrals or classical frequencies!

An interesting question is: Is it possible to keep the advantages of the two approaches while getting rid of their respective drawbacks? That is: Is it possible to obtain a Hamiltonian expression, which is precise enough at high energies and the interesting, physically meaningful features of which are nevertheless easily grabbed? Keeping in mind that the computation of a precise PES seems to be an unavoidable prerequisite, the question can again be formulated in the following way: Is it possible to derive from the computed PES this simple Hamiltonian expression, which is both precise at high energy and easy to analyze?

A possible answer to this question comes from the canonical perturbation theory derived by Birkhoff[18] and later extended by Gustavson[19] to take resonances properly into account. Gustavson's procedure explicitly enables one to rewrite a polynomial Hamiltonian in ''Birkhoff's normal form,'' that is, in a form such that the Poisson bracket of the second degree term (that is the sum of uncoupled harmonic oscillators) with any term of higher degree vanishes. As al-

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ready shown on several examples—two coupled harmonic oscillators,[20,21] the Henon–Heiles surface,[22,23] or the quadratic Zeeman effect in hydrogen,[24] Birkhoff–Gustavson perturbation theory (BGPT) enables one to obtain a reasonable approximation of these systems near the bottom of the well. Now, the interesting point is, that Birkhoff's normal forms happen to be just the simple Hamiltonians mentioned at the beginning of this section. More precisely, Birkhoff's normal form for a nonresonant system is the Dunham expansion, whereas for a resonant system (i.e., a system with rationally related fundamental frequencies) it is a single resonance Hamiltonian.

It is therefore tempting to use BGPT to simplify the analysis of highly excited vibrational systems. When doing so, one is, however, soon confronted with a well-known shortcoming of canonical perturbation theories, namely the divergence of the perturbative series. Let us be more precise about what divergence means in this context: Gustavson's procedure uses only well chosen canonical transformations, that is transformations of the phase space variables which preserve the form of Hamilton's equations. It operates on a polynomial Hamiltonian, and at each degree s of the theory, a canonical transformation is performed, which leaves the terms with degree lower than s unchanged, while the terms with degree s are put in Birkhoff's normal form. Usually, after the procedure has been applied up to a chosen degree, the terms with higher degree are simply dropped: this degree will be called the ''order'' of the procedure. For example, the x_{ij} spectroscopic parameters are obtained at fourth order of Gustavson's procedure, while the y_{ijk} parameters result from sixth order calculations. A naive conclusion is then that the higher the order of the perturbation calculations, the more precise the obtained approximation. This conclusion is, unfortunately, wrong: For a given set of levels, an increase in the order will most certainly first result in an increase in the precision of the frequencies calculated according to the approximate Hamiltonian, but at a given order the precision will start decreasing again and the divergence is then often very rapid (numerical examples will be given in the following sections of this paper). Moreover, it is not possible to predict at which order the precision will start to diverge, nor to guess what the optimal precision will be. The question is: what if the series diverges before the needed accuracy goal is achieved?

The aim of this paper is to show that a slight modification in BGPT can help going beyond the first divergences. That is, the divergence of the series is repelled to higher orders, while the accuracy of the approximate energy levels is further improved. This modification consists of using Gustavson's procedure, while dropping the requirement that the transformed Hamiltonian be in Birkhoff's normal form. Actually, the only point which needs to be modified is the definition of Gustavson's ''null space,'' whereas explicit calculations proceed along unaltered lines. Physically, this amounts to accepting that the approximate Hamiltonian might be a multiresonance one, instead of just a Dunham expansion or a single resonance Hamiltonian. The recent work of Beck *et al.*,[25] who were able to calculate variationally the energy values and the wave functions for about 1000 rotationless levels of phosphaethyne (HCP) from an *ab initio* potential energy surface (PES) at the multireference configuration interaction-complete active space self-consistent field (MRCI-CASSCF) level, will serve as a reference to illustrate this idea.

The remainder of this article is organized as follows: the principles of BGPT are outlined in Sec. II, paying special attention to dissociating Birkhoff's normal form from Gustavson's calculation procedure. The possibility of including more terms in the null space is put in evidence, thus leading to multiresonance Hamiltonians. Starting from the exact expression of kinetic energy in curvilinear internal coordinates and the *ab initio* PES of Beck *et al.*,[25] 361 levels of several transformed resonance Hamiltonians derived from up to 14th order perturbation calculations are then compared in Sec. III to the exact ones. The studied energy range extends up to more than half the dissociation energy value and involves up to 30 quanta in the bending motion. Convergence up to 13th order and an average absolute error as low as $2.2\ \mathrm{cm}^{-1}$ are reported for a two-resonance Hamiltonian, whereas the Dunham expansion converges only up to 4th order at an average error of $215\ \mathrm{cm}^{-1}$. Section IV is next devoted to a discussion of the limitations of this modified version of Gustavson's procedure. At last, the connections to other canonical perturbation theories, like Van Vleck or Lie transforms, are presented in Sec. V.

II. GUSTAVSON'S PROCEDURE AND BIRKHOFF'S NORMAL FORM

Let us first outline Gustavson's procedure,[19] while dropping every reference to Birkhoff's normal form.[18] To begin with, let us assume that the original polynomial Hamiltonian $H(p,q)$, where p is expressed in units of $\hbar$, has already been transformed up to degree $s-1$, where $s\geqslant 3$, and let us describe how it is transformed up to degree s according to Gustavson's procedure. In other terms, $s-3$ canonical transformations have already been performed, leading from the $(p,q)=(p^{(2)},q^{(2)})$ to the $(p^{(s-1)},q^{(s-1)})$ set of coordinates, such that

$$H(p,q)=\sum_{n=2}^{s-1}\Gamma^{(n)}(p^{(s-1)},q^{(s-1)})+\sum_{n\geqslant s}H^{(s-1,n)}(p^{(s-1)},q^{(s-1)}), \tag{2.1}$$

and one now looks for the next step, that is for the canonical transformation from $(p^{(s-1)},q^{(s-1)})$ to $(p^{(s)},q^{(s)})$, such that,

$$H(p,q)=\sum_{n=2}^{s}\Gamma^{(n)}(p^{(s)},q^{(s)})+\sum_{n\geqslant s+1}H^{(s,n)}(p^{(s)},q^{(s)}), \tag{2.2}$$

the goal being that $\Gamma^{(s)}$ contains only some given, chosen part $N^{(s)}$ of $H^{(s-1,s)}$, that is, of the term with degree s in the Hamiltonian transformed up to degree $s-1$:

$$\begin{aligned} H^{(s-1,s)}&=N^{(s)}+R^{(s)},\\ \Gamma^{(s)}&=N^{(s)}. \end{aligned} \tag{2.3}$$

In Eqs. (2.1) to (2.3), $\Gamma^{(n)}$, $H^{(s-1,n)}$, $H^{(s,n)}$, $N^{(n)}$, and $R^{(n)}$ are all homogeneous polynomes of degree n. We shall come

back later to the respective contents of the null space $N^{(s)}$ and the remainder $R^{(s)}$. Simple calculations[19–21] show that, whatever these contents are, the canonical transformation is obtained in the form of a generating function $W^{(s)}$

$$q_i^{(s)}=q_i^{(s-1)}+\frac{\partial W^{(s)}(p^{(s)},q^{(s-1)})}{\partial p_i^{(s)}},$$
$$p_i^{(s-1)}=p_i^{(s)}+\frac{\partial W^{(s)}(p^{(s)},q^{(s-1)})}{\partial q_i^{(s-1)}}, \tag{2.4}$$

computed as follows: $R^{(s)}$ is rewritten in terms of the classical analogs of the quantum ladder operators

$$a_i=\frac{1}{\sqrt{2}}\,(q_i+jp_i),$$
$$a_i^+=\frac{1}{\sqrt{2}}\,(q_i-jp_i). \tag{2.5}$$

The $(s-1)$ superscripts are omitted in Eq. (2.5). Each monomial $\Pi_k a_k^{l_k}(a_k^+)^{m_k}$ of the result is next divided by

$$j\sum_k\ \omega_k(l_k-m_k). \tag{2.6}$$

The result is then expressed back in the $(p^{(s-1)},q^{(s-1)})$ coordinates, and $p^{(s-1)}$ is finally replaced by $p^{(s)}$. Once this function $W^{(s)}$ has been computed, the homogeneous polynomes $H^{(s,n)}$ where $n>s$, that is the terms with degree higher than s in the Hamiltonian transformed up to degree s, are obtained according to

$$H^{(s,n)}(p,q)$$
$$=H^{(s-1,n)}(p,q)+\sum_{(i_1,i_2,\cdots)}\left(\frac{\partial^i H^{(s-1,m)}}{\Pi_k\partial p_k^{i_k}}\prod_k\left(\frac{\partial W^{(s)}}{\partial q_k}\right)^{i_k}\right.$$
$$\left.-\frac{\partial^i H^{(s-1,m)}}{\Pi_k\partial q_k^{i_k}}\prod_k\left(\frac{\partial W^{(s)}}{\partial p_k}\right)^{i_k}\right)\Big/\prod_k\ (i_k!), \tag{2.7}$$

where $i=\Sigma_k i_k$ and $m=n-i(s-2)$. The sum in Eq. (2.7) runs over all those values of $(i_1,i_2,\cdots)$ such that: $1\leqslant i\leqslant(n-2)/(s-2)$. (s) superscripts are again omitted in Eq. (2.7). Up to that point, the procedure involves no approximation: It is just a sequence of canonical transformations. The approximation eventually consists, after having transformed the original Hamiltonian up to a given degree, in neglecting all the terms with higher degree, thus retaining only the $\Gamma^{(s)}$'s.

Let us now come back to the contents of the null space $N^{(s)}$ and the remainder $R^{(s)}$. The result obtained by Birkhoff[18] is that the original Hamiltonian can be transformed into a Hamiltonian, which is a power series in one-dimensional uncoupled harmonic oscillators. For doing so, one just needs to require that the null space $N^{(s)}$ is obtained from $H^{(s-1,s)}$ expressed in terms of ladder operators by retaining only the monomials of the form $\Pi_k a_k^{m_k}(a_k^+)^{m_k}$. Using the canonical transformation to action-angle-like coordinates (I_k,φ_k),

$$I_k=\frac{1}{2}\,(p_k^2+q_k^2)=\frac{1}{2}\,(a_k a_k^++a_k^+a_k),$$
$$\tan\ \varphi_k=-\frac{p_k}{q_k}, \tag{2.8}$$

where the superscripts (s) are again omitted, one sees that the truncation at a given order leads precisely to the Dunham polynomial expansion in terms of the I_k's, which in this case are actually the action integrals of the motion. The fact that this series at best does not always converge[26] is easily grabbed by realizing that unconditional convergence would imply that all the systems are integrable and that chaos does not exist.

As worked out by Gustavson,[19] a further difficulty arises whenever the fundamental frequencies of the system satisfy an exact resonance condition, because of the division by the term in Eq. (2.6). For example, if modes 1 and 2 are in exact Fermi resonance, such that $\omega_1=2\omega_2$, then each monomial of $R^{(s)}$ in the form $a_1^m a_2^{+2m}\Pi_k a_k^{m_k}(a_k^+)^{m_k}$ (or its complex conjugate) would lead to a division by zero, whatever the values of m and the m_k's. The same conclusion holds for the Darling–Dennison resonance $\omega_1=\omega_2$ and the $a_1^m a_2^{+m}\Pi_k a_k^{m_k}(a_k^+)^{m_k}$ monomials. These monomials, therefore, ought to be put in the null space $N^{(s)}$, in order for the above procedure to work, leading, respectively, to a $m\varphi_1-2m\varphi_2$ and a $m\varphi_1-m\varphi_2$ angle dependence of the transformed Hamiltonian.

For these two possible definitions of the null space, corresponding to the nonresonant and resonant cases, the transformed Hamiltonians are said to be in Birkhoff's normal form, which just means that the Poisson bracket of each $\Gamma^{(s)}$ with the quadratic part of the Hamiltonian (that is, with the sum of the uncoupled harmonic oscillators) vanishes. This insures that each $\Gamma^{(s)}$ remains approximately a constant of the motion—or at least does not vary too much—as long as the quadratic part of the Hamiltonian dominates. While probably interesting in the context of the derivation of formal mathematical theories, this property is, however, of no help from a practical, physical point of view. More interesting is the fact that the transformed Hamiltonians remain integrable, as long as no more than one resonance condition is satisfied: this point has been used to assign approximate constants of the motion for classically chaotic vibrational dynamics.[22,23]

It is hoped that the presentation above clearly puts in evidence that the calculation procedure developed by Gustavson and the question of Birkhoff's normal form can be totally dissociated. In particular, it is stressed that *each different choice of* $N^{(s)}$ $(s\geqslant 3)$ *leads to a different approximation of the original Hamiltonian*. Of great importance is also the fact that *the convergence properties of these approximations are different*. For example, one can consider that in the extreme limit where $N^{(s)}$ is taken to be $H^{(s-1,s)}$, then the transformed Hamiltonian is just the original one and the procedure is convergent. Intuitively, the more terms are added in the null space, the closer the transformed Hamiltonian from the original one, and the better the convergence properties. But simultaneously, the more terms in the null space, the more complex and the less interesting the trans-

formed Hamiltonian. One can, however, try to play with the actual content of $N^{(s)}$, in order to get a precise yet simpler description of the original Hamiltonian. It should be noted—but this is of no practical consequence—that most of the time the transformed Hamiltonian is no longer in Birkhoff's normal form.

The two following sections of this work are aimed at showing that Gustavson's procedure with the modified definition of $N^{(s)}$ might be a powerful tool in the field of vibrational dynamics, and particularly in the study of highly excited vibrational states.

III. APPLICATION TO THE HIGHLY EXCITED VIBRATIONAL STATES OF HCP

A. Preliminary calculations

As stated in the Introduction, the recent work of Beck *et al.*,[25] who were able to calculate variationally the energy values and the wave functions for about 1000 rotationless levels of HCP from an *ab initio* potential energy surface (PES) at the MRCI-CASSCF level, will serve as a reference to illustrate this idea. However, since the canonical perturbation theory described in Sec. II applies only to polynomes with no first degree terms and with no second degree cross terms, one must first expand both the PES and the kinetic energy in Taylor series near an extremum. Then, Wilson's GF matrix formalism,[27] which is nothing but a first canonical transformation, has to be applied, in order to eliminate the second degree cross terms. These calculations are outlined in the present subsection.

The PES derived by Beck *et al.*[25] is expressed as a function V of the three coordinates R_1, R_2, and R_3, which stand, respectively, for the HC, CP, and HP separations. These coordinates are, however, not convenient for the Taylor expansion, since the minimum of V in the R_i coordinates is located at $-52\,547\ \mathrm{cm}^{-1}$ relative to the minimum of H+CP, that is $10\,316\ \mathrm{cm}^{-1}$ below the bottom of the well in Jacobi or in internal coordinates. Moreover, the values of the three bond lengths at the minimum are respectively $R_1=1.0173$, $R_2=1.5026$, and $R_3=3.5183$ Å, which is physically meaningless, since R_3 is necessarily smaller than the sum of R_1 and R_2. Jacobi or internal coordinates, which consist of two bond lengths and one angle, automatically take this condition into account, but the R_i coordinates do not.

One can also think of expanding V as a function of the deviations from equilibrium of the Jacobi coordinates r, R, and γ used by Beck *et al.* to diagonalize the quantum Hamiltonian matrix and to plot their figures. r is the CP bond length, R is the length from H to the center of mass G of the CP bond, and γ is the angle between HG and CP. γ is equal to zero in the linear equilibrium configuration HCP. The R_i's are expressed as

$$\begin{aligned} R_1&=\sqrt{\rho^2r^2+R^2-2\rho Rr\cos\gamma},\\ R_2&=r,\\ R_3&=\sqrt{(1-\rho)^2r^2+R^2+2(1-\rho)Rr\cos\gamma}, \end{aligned} \tag{3.1}$$

ρ being the ratio $m_P/(m_C+m_P)$ and m_P and m_C the masses of the phosphor and carbon atoms. Of course, one has to take care that all the values remain inside the convergence radius of each function when expanding V in Taylor series. In particular, the convergence radius of $\sqrt{x}$ is $0<x<2$, and it happens that for R_1 the expression below the square root sometimes becomes greater than 2 starting from about $15\,000\ \mathrm{cm}^{-1}$ above the bottom of the well. Since the goal is to take into account the levels up to $22\,000\ \mathrm{cm}^{-1}$ above the bottom, these coordinates are again not convenient.

In contrast, the usual curvilinear internal coordinates r_1, r_2 and α, where r_1 and r_2 are again just the HC and CP bond lengths and α is the HCP angle ($\alpha=\pi$ at equilibrium), are found to be a good set of coordinates. The R_i's are expressed in the form

$$\begin{aligned} R_1&=r_1,\\ R_2&=r_2,\\ R_3&=\sqrt{r_1^2+r_2^2-2r_1r_2\cos\alpha}, \end{aligned} \tag{3.2}$$

and all the values are found to remain inside the convergence radii of the square root, exponential and hyperbolic tangent functions up to $22\,000\ \mathrm{cm}^{-1}$ above the bottom of the well. V is thus expanded around the equilibrium values $r_1=1.0768$, $r_2=1.5581$ Å, and $\alpha=\pi$ at $E=-42\,231\ \mathrm{cm}^{-1}$ relative to H+CP. The vibrational part of the exact kinetic energy T

$$\begin{aligned} T=&\frac{1}{2}\left(\frac{1}{m_H}+\frac{1}{m_C}\right)p_{r_1}^2+\frac{1}{2}\left(\frac{1}{m_C}+\frac{1}{m_P}\right)p_{r_2}^2\\ &+\frac{\cos\alpha}{m_C}p_{r_1}p_{r_2}-\frac{\sin\alpha}{m_C}\left\{\frac{p_{r_1}}{r_2}+\frac{p_{r_2}}{r_1}\right\}p_\alpha\\ &+\frac{1}{2}\left\{\left(\frac{1}{m_H}+\frac{1}{m_C}\right)\frac{1}{r_1^2}+\left(\frac{1}{m_P}+\frac{1}{m_C}\right)\frac{1}{r_2^2}-\frac{2\cos\alpha}{m_Cr_1r_2}\right\}p_\alpha^2, \end{aligned} \tag{3.3}$$

where p_{r1}, p_{r2} and p_α are the momenta conjugate to the coordinates r_1, r_2 and α, is next expanded around the same equilibrium values. Since only the rotationless levels are considered in the work of Beck *et al.*,[25] the term dealing with the kinetic energy of the molecule rotating around the vanishing moment of inertia, which is called the vibrational angular momentum, is omitted in Eq. (3.3). Nonetheless, the double degeneracy of the bending motion is taken into full account in what follows. One is then left with two polynomes for V and T, the second degree terms of which are written in the form

$$T^{(2)}(P)+V^{(2)}(Q)=\tfrac{1}{2}P^+\cdot G\cdot P+\tfrac{1}{2}Q^+\cdot F\cdot Q, \tag{3.4}$$

where $Q=(\Delta r_2,\Delta\alpha,\Delta r_1)$ and $P=(p_{r2},p_\alpha,p_{r1})$, Δr_1, Δr_2, and $\Delta\alpha$ being the deviations of r_1, r_2, and α from equilibrium. G and F are symmetric but nondiagonal matrices. The point is, that Gustavson's procedure applies to polynomial Hamiltonians, the second degree of which is a sum of uncoupled harmonic oscillators, which can be written as

$$\Gamma^{(2)}(p,q)=T^{(2)}(p)+V^{(2)}(q)=\frac{1}{2\hbar^2}\,p^+\cdot\Omega\cdot p+\frac{1}{2}\,q^+\cdot\Omega\cdot q$$
$$=\sum_{i=1}^{3}\frac{\omega_i}{2}\left(\frac{p_i^2}{\hbar^2}+q_i^2\right), \tag{3.5}$$

where Ω is the diagonal matrix of the fundamental frequencies ω_i. The linear coordinate transformation from the (P,Q) to the (p,q) sets of conjugate coordinates is obtained according to Wilson's GF matrix formalism,[27] as follows: Let us call L the eigenvectors of the product matrix G.F. The products,

$$f=L^+\cdot F\cdot L,\qquad g=L^{-1}\cdot G\cdot(L^+)^{-1}, \tag{3.6}$$

are again diagonal, with eigenvalues f_i and g_i. Define now λ as the diagonal matrix with elements λ_i, such that

$$\lambda_i=\left(\frac{\hbar^2 g_i}{f_i}\right)^{1/4}. \tag{3.7}$$

The first canonical transformation, which is the link between Eqs. (3.4) and (3.5), is obtained as

$$Q=L\cdot\lambda\cdot q,\qquad P=((L\cdot\lambda)^+)^{-1}\cdot p, \tag{3.8}$$

and the fundamental frequencies ω_i are just

$$\omega_i=f_i\lambda_i^2=\hbar^2 g_i\lambda_i^{-2}=\hbar\sqrt{f_i g_i}. \tag{3.9}$$

It is worth noting that the (p,q) coordinates defined by Eq. (3.8) are ''normal coordinates,'' in the sense that they diagonalize the second degree terms of the vibrational Hamiltonian. However, they are not exactly the usual ''normal coordinates,'' since they are not linear combinations of Cartesian coordinates, but rather of true curvilinear internal coordinates. Also, it is interesting to notice that the initial choice of the r_1, r_2, and α set of coordinates leads to a transformation matrix L, which is close to unity. Indeed, the numerical value for L is

$$L=\begin{pmatrix}0.996 & 0 & 0.136\\ 0 & 1 & 0\\ -0.091 & 0 & 0.991\end{pmatrix}, \tag{3.10}$$

which means that the normal mode 1 is almost exactly the C–P stretching motion, the normal mode 2 is exactly the bending motion, and the normal mode 3 is essentially the C–H stretching motion.

B. The Dunham expansion

Calculation of the fundamental frequencies of HCP according to Eq. (3.9) leads to: $\omega_1\approx 1256$ (C–P stretch), $\omega_2\approx 650$ (bend), and $\omega_3\approx 3479\ \mathrm{cm}^{-1}$ (C–H stretch). No low order exact resonance condition is therefore fulfilled and, according to the original prescription by Birkhoff and Gustavson, the sole diagonal terms $\Pi_k a_k^{l_k}(a_k^+)^{l_k}$ ought to be put in the null space at each even order. The Hamiltonian is then obtained in the normal form

$$H_D=\sum_i\omega_i I_i+\sum_{i\leqslant j}x_{ij}I_iI_j+\sum_{i\leqslant j\leqslant k}y_{ijk}I_iI_jI_k+\cdots. \tag{3.11}$$

Each term with total degree n in the I_k coordinates is obtained at the degree $s=2n$ of BGPT. One is also reminded, that if the Hamiltonian has been put in normal form up to degree s, then the coordinates p and q in Eq. (3.8), as well as the corresponding ladder operators and the action integrals I_k, arise from $s-2$ canonical transformations. The superscripts (s) are simply dropped. The elements of the diagonal quantum Hamiltonian matrix in the harmonic oscillator basis are just

$$\langle v_1,v_2,v_3|H_D|v_1,v_2,v_3\rangle=\sum_i\omega_i n_i+\sum_{i\leqslant j}x_{ij}n_in_j+\sum_{i\leqslant j\leqslant k}y_{ijk}n_in_jn_k+\cdots, \tag{3.12}$$
$$n_1=v_1+\tfrac{1}{2}\quad n_2=v_2+1\quad n_3=v_3+\tfrac{1}{2},$$

which is the usual, well-known Dunham expansion. The vibrational angular momentum is assumed to be zero in Eqs. (3.11) and (3.12), as well as in the following expressions. If this were not the case, then only very slightly more complex expressions should be used.[28,29] The explicit numerical values for the parameters appearing in the expressions of the transformed Hamiltonians are not given in this article, because there are too many of them: 119 for the Dunham expansion at 14th order and 296 for $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ at the same order (see Sec. III D). Instead, the results will be presented as error tables. These tables give, for each Hamiltonian and each order of perturbation, the average absolute error, the root mean square (rms) error, and the maximum absolute error between the exact quantum levels relative to the ground state calculated by Beck *et al.*[25] and the levels of the transformed Hamiltonians, calculated using the matrix elements displayed throughout the text. The calculation of these errors further implies that one is able to associate each level of the exact Hamiltonian with one level of the transformed Hamiltonians. For this purpose, the assignments of Beck *et al.*[25] have been used. However, due to the strong Fermi resonance between the C–P stretch (mode 1) and the bend (mode 2), which will be put in evidence in this and the next subsections, the assignment according to only two quantum numbers plus one ordering integer has been chosen. The two quantum numbers are the number of quanta in the C–H stretch (v_3 in our notation, v_1 in Beck *et al.*'s notation) and the polyad number i. i is defined as

$$i=2v_1+v_2 \tag{3.13}$$

in our notation, and $i=2P=2v_2+2v_3$ in Beck *et al.*'s notation. The last good quantum number is destroyed by the Fermi resonance and is replaced by the order of the level within a given (v_3,i) polyad. At last, the levels of all the polyads with no level beyond 22 000 cm^{-1} above the bottom of the well ($i\leqslant 30$ for $v_3=0$, $i\leqslant 24$ for $v_3=1$, $i\leqslant 20$ for v_3

TABLE I. Accuracy of the levels of the Dunham expansion and the Fermi resonance Hamiltonians with one to three angles, obtained at perturbation orders increasing from 2 to 14. In each column, the sequence: average absolute/root mean square/maximum error (in cm^{-1}) between the exact quantum levels of HCP (Ref. 25) relative to the ground state and those of the transformed Hamiltonians is given. The 361 levels belonging to the complete polyads up to 22 000 cm^{-1} above the bottom of the well are included in the calculations. ''nc'' means ''not calculated,'' and ''idem'' that the result is identical to that in the previous column.

$H\rightarrow$ Order$\downarrow$	H_D	$H_D+H_F^{(1)}$	$H_D+H_F^{(1)}+H_F^{(2)}$	$H_D+H_F^{(1)}+H_F^{(2)}+H_F^{(3)}$
2	987/1122/2852	idem	idem	idem
3	987/1122/2852	987/1124/2852	idem	idem
4	215/441/2701	173/287/1341	idem	idem
5	215/441/2701	169/256/1011	idem	idem
6	706/1694/14433	21.0/40.0/235	20.9/40.3/245	idem
7	706/1694/14433	20.9/35.2/152	20.9/36.1/178	idem
8	7625/22262/226120	35.6/76.2/571	35.7/76.2/586	idem
9	7625/22262/226120	35.5/72.6/592	35.5/72.6/561	35.5/72.6/560
10	nc	10.8/36.7/395	10.6/33.2/350	10.6/33.2/350
11	nc	14.6/36.5/404	10.6/29.6/317	10.6/29.7/317
12	nc	20.7/47.8/397	19.8/52.2/564	19.8/52.1/561
13	nc	30.4/97.5/1161	19.7/51.3/563	19.7/51.2/559
14	nc	29.9/136/1870	13.1/58.0/749	13.1/58.0/749

$=2$, $i\leqslant 14$ for $v_3=3$, $i\leqslant 10$ for $v_3=4$, $i\leqslant 6$ for $v_3=5$, and $i=0$ for $v_3=6$) have been included in the calculation of errors, that is 361 out of the first 395 levels.

The results of error calculations for the Dunham expansion obtained from 3rd to 9th order BGPT are given in the second column of Table I. The line at order 2 corresponds to just the uncoupled harmonic oscillators. Orders 4 and 5 consist of the expansion up to the x_{ij} parameters, and orders 8 and 9 of the expansion up to the y_{ijkl} parameters. It is seen that the convergence of this model is very poor, being limited to 4th or 5th orders and an average absolute error of 215 cm^{-1}. At 8th order, the average absolute error has already diverged up to 7625 cm^{-1} (with a maximum error of 226 120 cm^{-1}!). It is therefore concluded that the Dunham expansion is very far from being sufficient for whatever quantitative purpose, despite there being no exact resonance in the HCP molecule.

C. The Fermi resonance Hamiltonian

The rapid divergence, which is observed for the Dunham expansion, can be traced back to the division by the small $\omega_1-2\omega_2\approx -44\ cm^{-1}$ factor, which occurs at third order in BGPT and leads to crudely overestimated values for some anharmonic parameters. For example, y_{122} and y_{123} are calculated, respectively, at 4.009 and $-6.628\ cm^{-1}$ for the Dunham expansion, whereas more probable values, obtained for the best two-resonance Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ in Sec. III D, are close to -0.073 and $0.167\ cm^{-1}$, and no 6th order parameter has an absolute value larger than $0.424\ cm^{-1}$! So the criterion of the normal form has to be abandoned, and the Fermi resonance must be taken into account despite its not being exact: this point is well known to the spectroscopists who need to fit spectra.[5–12] This involves a modification in the definition of the null spaces and leads to a non-normal form (according to the definition of Birkhoff) of the transformed Hamiltonian. As noted in Sec. II, Gustavson's procedure prescribes that all the monomials $a_1^m a_2^{+2m}\Pi_k a_k^{m_k}(a_k^+)^{m_k}$ (and their conjugate complexes) are included in the null space $N^{(s)}$ at order $s=3m+2\Sigma_k m_k$ in the case of an exact 1:2 resonance, because of the division by the term in Eq. (2.6). However, one can try to add the resonance terms one at the time for an approximate resonance, in order to check their influence and to get as simple a Hamiltonian as possible. The classical Hamiltonian is therefore obtained in the form

$$\begin{aligned} H&=H_D+\sum_{m\geqslant 1} H_F^{(m)},\\ H_F^{(m)}&=2I_1^{m/2}I_2^m\cos(m\varphi_1-2m\varphi_2)\\ &\quad\times\left(k^{(m)}+\sum_i k_i^{(m)}I_i+\sum_{i\leqslant j} k_{ij}^{(m)}I_iI_j+\cdots\right), \end{aligned} \tag{3.14}$$

and the additional nonzero matrix elements are

$$\begin{aligned} &\langle v_1,v_2,v_3|H_F^{(m)}|v_1-m,v_2+2m,v_3\rangle\\ &\quad=(-1)^m\left(k^{(m)}+\sum_i k_i^{(m)}n_i+\sum_{i\leqslant j} k_{ij}^{(m)}n_in_j+\cdots\right)\\ &\qquad\times\prod_{k=1}^{m}\{\sqrt{v_1-k+1}(v_2+2k)\},\\ &n_1=v_1-\frac{m-1}{2}\quad n_2=v_2+m+1\quad n_3=v_3+\frac{1}{2}. \end{aligned} \tag{3.15}$$

The expression in the right-hand side of Eq. (3.15) is not unique, and depends on the way the quantum operators are arranged during the quantization process. We shall come back to that point in Sec. IV C. Equation (3.15) shows that the $H_F^{(m)}$ terms only couple levels with the same values of v_3 and the polyad number i [Eq. (3.13)], which therefore remain good quantum numbers. The assignment to the levels calculated by Beck *et al.*[25] is thus again trivial. Concerning the classical picture of the molecule, it is worth noting that, despite the non-normal form, I_3 and $I=2I_1+I_2$ remain con-

stants of the motion, so that the system is integrable (nonchaotic): the last action integral is a function of the energy, I and I_3.

Error calculations are reported in the last three columns of Table I for the Fermi resonance Hamiltonians with one to three angles, that is explicitly for $H_D+H_F^{(1)}$, $H_D+H_F^{(1)}+H_F^{(2)}$ and $H_D+H_F^{(1)}+H_F^{(2)}+H_F^{(3)}$. It is seen that for the three of them the convergence is much better than for the Dunham expansion: at 7th order of Gustavson's procedure, the average absolute error is about 21 cm^{-1} and the maximum absolute error less than 180 cm^{-1}. Accuracy seems to diverge at 8th and 9th order, with an average absolute error of about 36 cm^{-1}, but it improves again somewhat unexpectedly at 10th order, with an average absolute error less than 11 cm^{-1}. A closer examination reveals that a majority of levels is calculated with a significantly smaller error at 10th order, but that the largest errors are also much larger at 10th order (about 600 cm^{-1}) than at 7th order, leading to close rms errors of about 36 cm^{-1}. Moreover, the Hamiltonian with two angles remains very close to the Hamiltonian with a single angle up to 10th order, whereas its divergence is slower at higher orders. Also, the differences between the two and three (or higher) angle Hamiltonians remain very small up to 14th order.

D. Two-resonance Hamiltonians

Now, what if average absolute errors of 21 or 11 cm^{-1} are still too large? Owing to the reduction of the average error by a factor of 10 or 20 upon addition of a single resonance in the definition of the null spaces, it is most probable that the error can be further reduced upon inclusion of other terms. However, this second step is far from being as obvious as the first one. Indeed the small offset $\omega_1-2\omega_2\approx-44\ \mathrm{cm}^{-1}$, together with the low 3rd order of Fermi resonance, made the choice of the first resonance unambiguous. The choice of the second resonance is not so clear. One can first think of a second small divisor problem, and look at small offsets appearing at low order, typically less than 7th order, in order to cancel the divergence observed at 8th order for the Fermi resonance Hamiltonians. There are only five of them below 450 cm^{-1}: $4\omega_1-2\omega_2-\omega_3\approx246$ (7th order), $3\omega_1-\omega_3\approx290$ (4th order), $2\omega_1+2\omega_2-\omega_3\approx334$ (5th order), $\omega_1+4\omega_2-\omega_3\approx379$ (6th order), and $6\omega_2-\omega_3\approx423\ \mathrm{cm}^{-1}$ (7th order). Among them, the most probable is by far the 1:3 close resonance between the C–P stretch and the C–H stretch, which is a 4th order coupling. The calculations are nevertheless not reported here, because it was found that this term changes the computed eigenvalues only very little. For example, the average/rms/maximum errors at 8th order and a single angle for the Fermi resonance are 36.0/76.5/572 cm^{-1}: this is even very slightly worse than in the third column of Table I, where the 1:3 resonance between the stretching motions is not taken into account. The other small offsets listed above were not checked, because a different approach proved to be much more efficient.

This approach relies on the observation that, for the Fermi resonance Hamiltonian with a single angle, the largest errors observed at 10th order of the theory are all associated with the lowest states of the highest polyads, like, for example, $(v_3,i)=(0,30)$, $(0,28)$, $(0,26)$, or $(1,24)$. In each case, the level of the Fermi resonance Hamiltonian is computed at a *lower* energy than the level of the exact Hamiltonian. Furthermore, these badly converged eigenvalues are extremely sensitive to the value of the 10th order parameter y_{22222}, so that the average/rms/maximum errors are reduced from 10.8/36.7/395 to 6.0/10.7/44.5 cm^{-1} as y_{22222} is *increased* from its original value ($-5.68\ 10^{-5}$) to $-4.20\ 10^{-5}\ \mathrm{cm}^{-1}$ (+26%). These eigenvalues are also quite sensitive to the 8th order parameter y_{2222}, while being much less sensitive to the values of all the other parameters. The conclusion one arrives at is that the badly converged levels are associated with almost pure bending motions and that the additional resonance one is looking for must principally result in an increase of the values of the y_{2222}, $y_{22222},\cdots$ parameters. It is to be noted that the bending character of the lowest lying states in high energy polyads was not obvious *a priori* and is a result of anharmonicities, since the negative offset $\omega_1-2\omega_2\approx-44\ \mathrm{cm}^{-1}$ shows that the levels with prominent bending character are the highest ones in low energy polyads.

The lowest order coupling with the strongest effect on y_{2222} (and so on) one can think of is obtained upon inclusion of the $a_2^{2m}\Pi_k a_k^{m_k}(a_k^+)^{m_k}$ monomials (and their conjugate complexes) in the null spaces. If the Fermi coupling is meant to be a "$\omega_1\approx2\omega_2$" resonance, then this additional coupling might be described as a "$2\omega_2\approx0$" resonance, despite the rather large value $2\omega_2\approx1301\ \mathrm{cm}^{-1}$! More precisely, the classical Hamiltonian is obtained in the form

$$H=H_D+\sum_{m\geqslant1}H_F^{(m)}+\sum_{m\geqslant1}H_C^{(m)},$$
$$H_C^{(m)}=2I_2^m\cos(2m\varphi_2)\left(\sum_i\kappa_i^{(m)}I_i+\sum_{i\leqslant j}\kappa_{ij}^{(m)}I_iI_j+\cdots\right), \tag{3.16}$$

and the additional nonzero matrix elements are

$$\langle v_1,v_2,v_3|H_C^{(m)}|v_1,v_2+2m,v_3\rangle$$
$$=(-1)^m\left(\sum_i\kappa_i^{(m)}n_i+\sum_{i\leqslant j}\kappa_{ij}^{(m)}n_in_j+\cdots\right)$$
$$\times\prod_{k=1}^{m}(v_2+2k),$$
$$n_1=v_1+\frac{1}{2}\quad n_2=v_2+m+1\quad n_3=v_3+\frac{1}{2}. \tag{3.17}$$

According to Eqs. (3.16) and (3.17), $H_C^{(m)}$ couples levels with the same number v_3 of quanta in the C–H stretch, but with different values i and $i\mp2m$ of the polyad number. Consequently, v_3 is the last good quantum number. From the classical point of view, the system is no longer integrable, but chaos cannot be generalized, due to I_3, which remains the last action integral. The fact that the polyad number i is no longer a good quantum number causes the assignment of the levels of the two-resonance Hamiltonians in Eqs. (3.16) and (3.17) to become somewhat less straightforward than for the Fermi resonance Hamiltonian in the previous subsection. Polyads are, however, not heavily mixed, and the following

TABLE II. Accuracy of the levels of two resonance Hamiltonians, obtained at perturbation orders increasing from 6 to 14. In each column, the sequence: average absolute/root mean square/maximum error (in cm^{-1}) between the exact quantum levels of HCP (Ref. 25) relative to the ground state and those of the transformed Hamiltonians is given. The results for the two-resonance Hamiltonians are presented in the columns labeled (1) and (2), whereas the results for the Fermi resonance Hamiltonians with one and two angles—but with the same parameters as, respectively, in columns (1) and (2)—are presented in the last two columns. The 361 levels belonging to the complete polyads up to 22 000 cm^{-1} above the bottom of the well are included in the calculations.

$H\rightarrow$ Order$\downarrow$	$H_D+H_F^{(1)}+H_C^{(1)}$ (1)	$H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ (2)	$H_D+H_F^{(1)}$ Parameters of (1)	$H_D+H_F^{(1)}+H_F^{(2)}$ Parameters of (2)
6	30.4/60.9/608	30.9/61.0/601	35.1/63.4/611	35.4/63.5/605
7	28.7/55.5/524	29.4/56.2/532	33.5/58.2/529	34.1/58.9/537
8	11.0/33.1/397	11.5/32.9/388	15.5/33.8/372	15.9/33.6/364
9	9.0/19.8/195	8.1/21.8/282	14.5/23.0/179	13.8/24.6/263
10	5.9/11.0/46.0	4.4/8.0/48.6	9.5/13.8/54.6	8.3/11.0/47.8
11	8.1/20.3/191	4.4/9.3/76.5	10.8/22.5/207	8.1/11.1/84.8
12	9.3/26.2/304	2.6/11.5/197	11.3/25.8/215	6.9/12.5/133
13	29.8/129/1631	2.2/10.8/188	30.6/109/1415	6.6/11.4/120
14	29.4/108/1533	4.0/15.7/205	30.8/112/1481	7.7/16.8/203

automatic assignment procedure was found to work very well: For each normalized eigenvector $\psi^{(n,v_3)}$ associated with the nth level with v_3 quanta in the C–H stretch

$$\psi^{(n,v_3)}=\sum_{v_1,v_2} c_{v_1,v_2}^{(n,v_3)}|v_1,v_2,v_3\rangle, \tag{3.18}$$

a vector $P^{(n,v_3)}$ of the contribution of each polyad to the level is computed, according to

$$P_i^{(n,v_3)}=\sum_{2v_1+v_2=i} c_{v_1,v_2}^2. \tag{3.19}$$

Afterward, polyads i are filled one at a time, starting from the lowest one $(i=0)$, by arranging the so-far unassigned levels in descending order of the ith component of their $P^{(n,v_3)}$ vectors and in retaining for the polyad i the first $\mathrm{Int}(i/2+1)$ levels in the list [$\mathrm{Int}(x)$ is just the integral part of x and $\mathrm{Int}(i/2+1)$ is the number of levels in polyad i].

Error calculations are reported in Table II for the two-resonance Hamiltonians $H_D+H_F^{(1)}+H_C^{(1)}$ and $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$. The 8th order divergence is canceled for both of them, and perturbation calculations converge at least up to 10th order. At 10th order, the average/rms/maximum errors are 5.9/11.0/46.0 for the former, and 4.4/8.0/48.6 cm^{-1} for the latter, very close to the optimal values (6.0/10.7/44.5 cm^{-1}) obtained following the correction ''by hand'' of y_{22222}. However, y_{22222} is calculated at about $-8.6\ 10^{-6}$ cm^{-1} for the two-resonance Hamiltonians, against $-4.20\ 10^{-5}$ cm^{-1} for the value corrected by hand. This shows that, as was to be expected, the change in parameters due to the consideration of the ''$2\omega_2=0$'' resonance is more complex than the sole increasing of the y_{22222} parameter. The Hamiltonian with a single angle for the Fermi resonance then diverges again rather sharply starting from the 11th order: at 13th order the average/rms/maximum errors are again as high as 29.8/129/1631 cm^{-1}. In contrast, the Hamiltonian with two angles for the Fermi resonance goes on converging up to 13th order, with an average absolute error of about 2.2 cm^{-1}, that is about five times better than for the better Fermi resonance Hamiltonian. Interestingly, the error distribution is highly singular: all the levels, except for three of them, are calculated with an error smaller than 13 cm^{-1}. The three exceptions are the first and third levels of the polyad $(v_3,i)=(0,30)$, with respective errors of 188 and 28.4 cm^{-1}, and the first level of the polyad $(v_3,i)=(0,28)$, with an error of 62.1 cm^{-1}, that is again the lowest levels of the highest polyads. The fact that the better results obtained for the two-resonance Hamiltonians compared to the Fermi resonance Hamiltonians are most of all due to the correction of the parameters of the Fermi resonance Hamiltonian rather than to the interpolyad coupling by itself, can be further proved by calculating the levels of HCP using the Fermi resonance Hamiltonians in Eqs. (3.14) and (3.15), but the parameters ω, x, y, and k computed for the two-resonance Hamiltonians in Eqs. (3.16) and (3.17). The result is given in the last two columns of Table II. Despite the slight deterioration of the average absolute error for the Fermi resonance Hamiltonian with two angles, the discussion above remains mostly unchanged, whether the off-diagonal coupling in Eq. (3.17) is taken into account or not. Finally, it should be noted, in agreement with the previous subsection, that $H_F^{(3)}$ and higher order Fermi couplings have almost no influence on the computed eigenstates.

IV. DISCUSSION

With an average absolute error as good as 2.2 cm^{-1} and an average relative error of about 0.014% for 361 levels up to 22 000 cm^{-1} above the bottom of the well, and with up to 30 quanta in the bending degree of freedom, the transformed Hamiltonians presented in the previous section are considered to be good approximations of the exact $T+V$ Hamiltonian. Yet, they are much easier to handle than the exact one, thanks to the remaining good quantum numbers and action integrals. Some advantages of the transformed resonance Hamiltonians are easily grabbed. For example, from the technical point of view, the calculation of the eigenstates requires the diagonalization of matrices less than 190 times

190, which is achieved without any particular programming care. In contrast, the diagonalization of the exact Hamiltonian involves basis sizes as large as a few thousands and cannot be performed without the help of such sophisticated tools as highly contracted/truncated basis sets.[30] Another obvious advantage of the transformed Hamiltonians consists of the immediate assignment of the levels, thanks to the remaining good quantum number v_3 and the moderate mixing of the polyads with different values of i. This again contrasts with the assignment of the levels of the exact Hamiltonian, which requires a visual examination of 2D projections and 3D representations of the wave functions.[25] Further advantages of resonance Hamiltonians, connected with the calculation of classical quantities, will become clearer in a forthcoming article dedicated to the description of the classical dynamics of HCP at high vibrational energies[31] by means of the resonance Hamiltonians derived in the present article. In the remainder of this paper, the limitations of this approach will instead be presented.

A. Validity of the model

The number v_3 of quanta in the C–H stretch and the polyad number i remain good quantum numbers for the Fermi resonance Hamiltonians in Eqs. (3.14) and (3.15). Therefore, the calculation of eigenstates is performed for one polyad (v_3,i) at a time, and involves the diagonalization of a finite square matrix of size $\mathrm{Int}(i/2+1)$. In contrast, i is no longer a good quantum number for the two-resonance Hamiltonians in Eqs. (3.16) and (3.17), because the $H_C^{(m)}$ terms couple levels with different values of i. Therefore, the matrix to be diagonalized is *a priori* infinite for each value of v_3. What is hoped, is that the computed eigenvalues depend only very slightly on the size of the basis. To check this point, the following calculations were performed: Let us call $i_{\max}(v_3)$ the highest polyad one wants to compute for each value of v_3 (for example, $i_{\max}=30$ for $v_3=0$, see Sec. III B). The Hamiltonian matrices which led to the results in Table II were built, for each value of v_3, in a basis which includes all the vectors $|v_1,v_2,v_3\rangle$, such that v_2 is even and $i=2v_1+v_2\leqslant i_{\max}+6$ instead of just $i_{\max}$ (this basis contains 190 vectors). The validity of these calculations is now checked by varying the number n of polyads, which are added to $i_{\max}$ ($n=6$ for the results in Table II). The results for the two-resonance Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ are presented in Table III in the form of error calculations, for perturbation orders increasing from 11 to 14 and n increasing from 4 to 12. It is seen that the size of the basis has virtually no influence on the average absolute error and a limited effect on the maximum error (and hence on the rms error) up to the 13th order of perturbation. In contrast, the average absolute error varies from 3.6 to 4.5 cm^{-1} and the maximum error from 150 to 402 cm^{-1} at 14th order of perturbation theory. It was verified, using a different, more sophisticated method for assigning quantum numbers to each energy level, that this conclusion does not depend on the assignment procedure. The same results are presented in Table IV for the two-resonance Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}+H_C^{(2)}$ and for perturbation orders increasing from 8 to 11. For this Hamiltonian, the results are seen to remain stable with respect to the basis size only up to 9th order, whereas 10th order calculations already fluctuate too much. What physically happens with the results that are not satisfactory, is that the levels of additional higher polyads lie in the same energy range as those of lower polyads and interact all the more strongly with them as the order of the perturbation is increased. For sufficiently strong couplings, the addition of a single high energy polyad will therefore displace in series the coupled levels of lower energy polyads. Stated in other words, the model of a resonance type Hamiltonian built on a harmonic basis is no longer valid at sufficiently high perturbation orders and/or at sufficiently high vibrational energies, the limit of validity depending on the exact expression of the Hamiltonian.

TABLE III. Checking for the stability of the computed levels of $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$, at perturbation orders increasing from 11 to 14. n is the number of additional polyads included in the basis set. In each column, the following sequence is given: average absolute/root mean square/maximum error (in cm^{-1}) between the exact quantum levels of HCP (Ref. 25) relative to the ground state and those of the two-resonance Hamiltonian. The 361 levels belonging to the complete polyads up to 22 000 cm^{-1} above the bottom of the well are included in the calculations.

Order n	11	12	13	14
4	4.4/9.4/77.0	2.6/11.3/189	2.2/10.4/180	3.6/12.2/150
6	4.4/9.3/76.5	2.6/11.5/197	2.2/10.8/188	4.0/15.7/205
8	4.3/9.3/76.0	2.7/12.8/222	2.3/12.1/214	4.5/24.0/402
10	4.3/9.3/73.1	2.7/11.3/189	2.3/10.5/180	4.1/15.8/174
12	4.3/9.4/76.7	2.6/11.8/202	2.3/11.1/194	4.4/23.1/383

B. Difficulties in further lowering the error

The agreement between the exact and transformed Hamiltonians presented above is felt to be sufficient in most practical cases. Let us recall that average/rms/maximum errors as small as 9.5/13.8/54.6 cm^{-1} (4th column of Table II) are obtained for the very simple 10th order $H_D+H_F^{(1)}$ Hamiltonian using the parameters of $H_D+H_F^{(1)}+H_C^{(1)}$, and that these errors are lowered to 2.2/10.8/188 cm^{-1} (3rd column of Table II) for the slightly more complex $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ Hamiltonian at 13th order. Several attempts were made to further diminish this error, but the task proved to be difficult for various reasons. As mentioned in Sec. III D, the three badly converged levels of the most precise two-resonance Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ are the lowest levels of the highest polyads, that is the levels with the most pronounced bending character. Therefore, the off-diagonal coupling which has to be added to further lower the

TABLE IV. Same as Table III, but for the Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}+H_C^{(2)}$ and perturbation orders increasing from 8 to 11.

Order n	8	9	10	11
4	9.6/22.8/207	5.8/11.8/130	3.9/9.2/133	2.9/7.0/104
6	9.6/22.7/205	5.7/11.8/128	4.6/16.2/219	3.1/10.5/183
8	9.5/22.6/200	5.7/11.7/125	4.0/11.0/166	3.4/12.6/216
10	9.5/22.5/198	5.7/11.6/124	3.7/7.1/72.8	2.9/6.0/56.7
12	9.5/22.4/194	5.7/11.4/121	4.0/9.1/111	3.0/6.8/81.9

error, certainly corrects the anharmonic parameters with prevalent bending character. The most probable couplings are then built on the symmetry allowed monomials $a_2^4, a_1 a_2^2, a_2^2 a_3^+, a_2^2 a_3$ and their conjugate complexes, and are associated, respectively, with the angles $4\varphi_2, \varphi_1+2\varphi_2$, and $\varphi_3 \mp 2\varphi_2$. The first possibility is just $H_C^{(2)}$, which was shown in the previous subsection to lead to a prematurely invalid model at 10th order of perturbation theory. The addition of the next angle $\varphi_1+2\varphi_2$, while not suffering from the same drawback, just does not increase significantly the accuracy of the computed levels. A different problem was encountered while trying to include the last two angles $\varphi_3 \mp 2\varphi_2$. Namely, the coupling between the vectors $|v_1,v_2,v_3\rangle$ and $|v_1,v_2+2,v_3\mp 1\rangle$ of the harmonics basis happens to be so large that neither v_3 nor i remain, even approximately, good quantum numbers. The first consequence is that the simple assignment procedure of Sec. III D is by far insufficient. Most certainly, this is not a serious drawback, and one could think of a slightly more complex scheme to assign the levels. But the game is not worth the candle, for the simple reason that the resulting resonance Hamiltonian has lost most of its other advantages compared to the exact $T+V$ expression anyway: from the quantum point of view, there remain no good quantum numbers at all and the Hamiltonian matrices are no longer of small size. In the same way, there remains no classical constant of the motion, and the study of the dynamics at high vibrational energies is then no longer simpler for the resonance Hamiltonian than for the exact one.

C. The influence of the quantum matrix elements

Gustavson's procedure transforms a classical, polynomial Hamiltonian in $(p,q)=(p^{(2)},q^{(2)})$ coordinates into another classical, polynomial Hamiltonian in $(p^{(s)},q^{(s)})$ coordinates. When expressed in terms of the action-angle-like coordinates of Eq. (2.8), the transformed Hamiltonians are those given in Eq. (3.11) for the Dunham expansion, in Eq. (3.14) for the Fermi resonance Hamiltonian, and in Eq. (3.16) if the "$2\omega_2=0$" resonance is also taken into account. Calculation of energy levels, and therefore the computation of the quantum matrix elements in Eqs. (3.12), (3.15), and (3.17), further requires that explicit quantization rules are assumed, for the simple reason that quantum p_k and q_k operators, as well as creation and annihilation operators, do not commute. This problem is not simple and will not be treated here. For a discussion of the quantization of Birkhoff–Gustavson's normal forms, the reader is referred to the works of Robnik,[32] Ali,[33] Eckhardt,[34] and Fried and Ezra.[35] What we want to stress instead, is that the question of the explicit correspondence, which is assumed between a classical polynome and its quantum counterpart, might anyway make the definition of more accurate resonance Hamiltonians at best ambiguous. Since Weyl's correspondence rules, which are sometimes claimed to be the "best" ones,[36] result in an explosion of the number of expressions to handle,[32] this idea will be illustrated using three easier correspondence rules, which are some kinds of symmetrized versions of Robnik's rules.[32]

TABLE V. The influence of the explicit form of quantum matrix elements. In each column, the following sequence is given: average absolute/root mean square/maximum error (in cm^{-1}) between the exact quantum levels of HCP (Ref. 25) relative to the ground state and those of $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ obtained at perturbation orders increasing from 6 to 13. The explicit quantum matrix element corresponding to each classical monomial varies from column 2 to 4 (see Sec. IV C). The third column of this table is identical to the third column of Table II and has been copied for convenience. The 361 levels belonging to the complete polyads up to 22 000 cm^{-1} above the bottom of the well are included in the calculations.

Order↓	"left"	"sym"	"right"
6	31.4/62.1/608	30.9/61.0/601	30.5/60.1/594
7	30.1/58.0/544	29.4/56.2/532	29.2/54.8/520
8	13.4/34.6/387	11.5/32.9/388	10.5/31.4/388
9	8.5/21.5/273	8.1/21.8/282	8.7/22.4/289
10	4.6/8.6/62.6	4.4/8.0/48.6	5.5/9.0/46.1
11	5.4/11.5/100	4.4/9.3/76.5	5.0/8.3/48.8
12	3.3/8.6/128	2.6/11.5/197	4.5/18.6/323
13	3.2/7.8/116	2.2/10.8/188	4.4/18.1/317

First of all, the quantum operators associated with the monomials $\Pi_k a_k^{l_k}(a_k^+)^{l_k}$ of the Dunham expansion are taken to be

$$\prod_k \frac{1}{2^{l_k}} \underbrace{(a_k a_k^+ + a_k^+ a_k)\cdots(a_k a_k^+ + a_k^+ a_k)}_{l_k \text{ times}}. \tag{4.1}$$

The polynomial expansions in $k^{(m)}$ and $\kappa^{(m)}$, which appear in $H_F^{(m)}$ and $H_C^{(m)}$ and which we call generically d, are handled along the same lines as in Eq. (4.1). Let us further call *ofd* the purely off-diagonal couplings, where the raising operator acts on mode 2, that is explicitly, $ofd=a_1^m a_2^{+2m}$ for $H_F^{(m)}$ and $ofd=a_2^{+2m}$ for $H_C^{(m)}$. Three possible choices of correspondence rules for $H_F^{(m)}$ and $H_C^{(m)}$, which lead to Hermitian matrices with simple elements, are

$$\begin{aligned} &\text{left}=d\circ ofd+ofd^*\circ d,\\ &\text{right}=d\circ ofd^*+ofd\circ d,\\ &\text{sym}=\tfrac{1}{2}\,(\text{left}+\text{right}), \end{aligned} \tag{4.2}$$

where ofd^* denotes the operator conjugate to *ofd* (it is remembered that d is self conjugate). The later symmetrized arrangement "sym" was actually assumed in Eqs. (3.15) and (3.17). For the two other choices, the sole values of n_1 and n_2 need to be changed in these equations. For the "left" arrangement, one obtains

$$\begin{aligned} &n_1=v_1-m+\tfrac{1}{2} \quad n_2=v_2+2m+1 \quad \text{in Eq. (3.15)},\\ &n_1=v_1+\tfrac{1}{2} \quad n_2=v_2+2m+1 \quad \text{in Eq. (3.17)}, \end{aligned} \tag{4.3}$$

and for the "right" arrangement the result is

$$n_1=v_1+\tfrac{1}{2} \quad n_2=v_2+1 \quad \text{in Eqs. (3.15) and (3.17)}. \tag{4.4}$$

The errors between the exact levels of Beck *et al.*[25] and the levels of the two-resonance Hamiltonian $H_D+H_F^{(1)}+H_F^{(2)}+H_C^{(1)}$ computed according to the three quantization procedures mentioned above are presented in Table V. While the

general trends of the convergence properties are identical for the three of them for increasing values of the order of perturbation, it is seen that the errors vary largely at the highest orders. For example, at 13th order, the average/rms/maximum errors are, respectively, 3.2/7.8/116 for the ''left'' arrangement and 4.4/18.1/317 cm^{-1} for the ''right'' arrangement, compared to 2.2/10.8/188 cm^{-1} for the symmetrized sum. It is therefore most likely that any further refinement of the resonance Hamiltonian, which will be obtained at orders probably greater than, say, 11 to 13, will depend on the precise quantization rules which are assumed. One might then wonder about the physical interest in pursuing calculations further.

V. CONNECTIONS TO OTHER CANONICAL PERTURBATION THEORIES

This section contains a comparison with the results obtained using two other canonical perturbation theories, namely the Van Vleck perturbation theory (CVPT) and the classical Lie operator based perturbation theories (LOPT's). Actually, CVPT and LOPT are closely related, and classical LOPT's,[35,37–43] specially Dragt–Finn perturbation theory,[35,39–41] mostly involve replacing quantum commutators by classical Poisson brackets in quantum CVPT.[44–49] Also, a new method,[50] which can be viewed as a specific case of a more general work[51,52] and is called mixed diagonalization, has recently been introduced, in which an effective Hamiltonian operator acting on a reduced dimensional space is constructed using the same similarity transformations of CVPT. Detailed descriptions of these methods will not be presented here, the interested reader being referred to the articles listed above, but it is noted that strong similarities also exist between LOPT or CVPT and BGPT: indeed, the null space $\Gamma^{(s)}$ in BGPT plays the same role as the transformed Hamiltonian $K_n^{(n)}(n=s-2)$ in CVPT, and the remainder $R^{(s)}$ as the operator $S^{(n)}$ associated with the unitary transformation $\exp(i\lambda^n[S^{(n)},])$ (the notations here are those of Sibert[48,49]).

The point that is common to all these methods and contrasts with those based on generating functions like Gustavson's procedure, is that the coordinate transformations are linear, so that the inversion of equations to express ''new'' coordinates in terms of ''old'' ones is trivial. This is often presented as a decisive advantage of LOPT and CVPT compared to BGPT. It should, however, be noted that Gustavson's procedure leads directly to an expression of the Hamiltonian in the new coordinates, so that inversion is not required for the computation of eigenstates. It is only when more precise results are wanted, like, for example, the calculation of infrared transition intensities, that this inversion must be performed, in order to compute the dipole operator in the new coordinates. This is probably not an insuperable task from the computational point of view, but it is true that the proof remains to be given that this can be done for Gustavson's procedure, whereas such results have already been obtained using CVPT.[53–56] On the other hand, one can argue that linear transformations are perhaps not the best suited ones for studying PES's far above the bottom of the well, and that allowing for a polynomial dependence between new and old coordinates might be more adapted to the curvature of the PES. For example, we have shown that levels of HCP with up to 30 quanta in the bending degree of freedom, corresponding to something like a 240° amplitude of motion, can be reproduced with an error lower than 55 cm^{-1} using Gustavson's procedure, whereas no such result has ever been published for CVPT—which again does not mean that CVPT is unable to meet this standard.

Concerning the quantization of the classical normal form, the problem is just the same for LOPT's[35] and Gustavson's procedure.[32–34] In contrast, the Van Vleck transformations, be they performed in the matrix representation or in the operator representation,[48,49,57,58] correctly treat the ordering of the operators, so that one does not have to invoke Weyl's correspondence rules. The operator representation has the prominent advantage compared to the matrix representation, that it leads to an analytical expression for the transformed Hamiltonian, so that its classical and semiclassical properties can be investigated,[59] just like upon use of Gustavson's procedure.[20–24,28,29,31] It is to be noted that a key feature for applying CVPT to the study of real molecules[49,59–65] is that all the operators be reexpressed in the same form, in order to both reduce the space required to store the transformed Hamiltonian and to simplify the evaluation of all the commutators. The convention, which is usually assumed,[48] is that the lowering operators act first and the raising operators act second... which happens to be the quantization rule proposed by Eckhardt[34] to quantize the classical BGPT normal forms.

Let us now consider the question of the shape of the transformed Hamiltonian, that is of the resonances, which are explicitly taken into account. What is clear is that physicists who use CVPT have long recognized the importance of taking some resonances explicitly into account, even though they are not exact. However, except in one case,[62] the strategy adopted for the definition of the transformed Hamiltonian is different from that presented in this article, because the underlying purpose is also different. Indeed, our main interest is in the classical, dynamical properties of the molecular system. Therefore, the number of resonances that are taken into account must be as small as possible, for the reasons outlined in Sec. IV B. In contrast, the main goal of the people who use CVPT is to spare computer time. This is achieved by requiring that the transformed Hamiltonian have one or several good quantum numbers left. For example, the last good quantum number is taken to be $2v_1+v_2+v_3+v_4+2v_5+v_6$ for H_2CO,[49,62,63] $2v_1+v_2+2v_3$ for H_2O and its deuterated derivatives[60] and SO_2,[63] $2v_1+v_2+4v_3$ for CO_2,[61] $2v_1+v_2+3v_3+v_4$ for AlF_3,[65] and $3v_1+v_2+4v_3+v_4$ for SiF_3.[65] What CVPT does is to transform the initial coordinates to new coordinates, such that, except for neglected higher order terms, the linear combinations above remain good quantum numbers for the Hamiltonian expressed in the new coordinates. That is, the Hamiltonian matrix in the new coordinates is block diagonal and each block can be diagonalized separately, thereby largely reducing the computer time. However, the exact content of the blocks has a much more limited influence on the speed of the numerical calculations, so that actually *all the*

resonances coupling levels with the same value of the remaining good quantum number were retained in the transformed Hamiltonians for the molecular systems listed above. For instance, the basic resonances for water are the Fermi resonance between the symmetric stretch and the bend, that is $a_1^+ a_2^2 + hc$, and the Darling–Dennison resonance between the symmetric and the asymmetric stretches, that is $a_1^{+2} a_3^2 + hc$. However, the transformed Hamiltonian discussed in Ref. 60 contains low order additional terms like $a_1 a_2^2 a_3^{+2} + hc$, which also couple only basis levels with the same values of $2v_1 + v_2 + 2v_3$. But again, these differences between Sibert *et al.*'s work and this one result mostly from different strategies inspired by different goals. CVPT could have been used to derive a Hamiltonian similar to Eqs. (3.16) and (3.17) for HCP (whether the corresponding values of the spectroscopic parameters lead to a better or a worse accuracy remains an open question). This is actually what was done in the exception mentioned above,[62] where it was shown that two resonances were necessary, but also sufficient, to compute with a good accuracy the intensity of a few infrared transitions of HCN.

In conclusion, it is the first time that so many levels are computed for a realistic molecular system using so few resonances, which makes HCP a fine benchmark for the comparison of the respective capabilities of LOPT's, CVPT, and Gustavson's procedure, which is asked for by many authors.

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