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Criteria for first- and second-order vibrational resonances and correct evaluation of the Darling-Dennison resonance coefficients using the canonical Van Vleck perturbation theory

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The second-order vibrational Hamiltonian of a semi-rigid polyatomic molecule when resonances are present can be reduced to a quasi-diagonal form using second-order vibrational perturbation theory. Obtaining exact vibrational energy levels requires subsequent numerical diagonalization of the Hamiltonian matrix including the first- and second-order resonance coupling coefficients. While the first-order Fermi resonance constants can be easily calculated, the evaluation of the second-order Darling-Dennison constants requires more complicated algebra for seven individual cases with different numbers of creation-annihilation vibrational quanta. The difficulty in precise evaluation of the Darling-Dennison coefficients is associated with the previously unrecognized interference with simultaneously present Fermi resonances that affect the form of the canonically transformed Hamiltonian. For the first time, we have presented the correct form of the general expression for the evaluation of the Darling-Dennison constants that accounts for the underlying effect of Fermi resonances. The physically meaningful criteria for selecting both Fermi and Darling-Dennison resonances are discussed and illustrated using numerical examples. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4903927]

I. INTRODUCTION

Significant advances in applying variational solutions to vibrational and vibration-rotational problems using advanced methods[1–3] have demonstrated very high accuracy in a purely *ab initio* prediction of vibrational and vibration-rotational spectra. However, at present these methods are limited to small and highly symmetric molecules because such methods require detailed knowledge of the global potential energy surface (PES) far from the equilibrium minima. In turn, quantum-mechanical evaluation of a global PES requires calculations on huge spatial grids and the application of complex forms of Hamiltonians with curvilinear coordinates.[4] In addition, the size of the basis set dramatically grows by an order of magnitude with the addition of each new atom.

An alternative quantum-mechanical method of modeling nuclear motion, anharmonic second-order vibrational perturbation theory (VPT2) requires a Taylor expansion of electronic energy in powers of rectilinear normal coordinates at the point of equilibrium, truncated at the fourth order. Since many established quantum-mechanical methods (such as MP2 or DFT) provide analytic second derivatives of the energy, the necessary expansion coefficients can be obtained by single and double numerical differentiation of Hessians calculated at displaced configurations. Moreover, quartic force constants with four different indices do not markedly contribute to anharmonic corrections and can often be omitted (they only contribute to certain types of Darling-Dennison constants). Such a representation of a PES is usually called "semi-diagonal" and provides a good compromise for many applications.[5]

The success of VPT2 in predicting anharmonic energy levels up to rather high levels of excitation is partly explained by the fact that VPT2 treatment provides an exact solution for the Morse potential.[6,7] Matthews *et al.*[8] wrote: "The fact that VPT2 is exact for the Morse oscillator is surprisingly poorly appreciated in the theoretical chemistry community." Another advantage of VPT2 is the fact that closed-form solutions are available for the anharmonic constants.[9–15] Accounting for the first-order Fermi and the second-order Darling-Dennison resonance couplings is performed by diagonalizing small-sized and sparse matrices, whose matrix elements can also be evaluated using closed-form expressions.[11,12,16–20] If a molecule is not too large and the form of its polyad vector can be identified,[21–26] the matrix representation of the Hamiltonian becomes particularly suitable, as the matrix gains the convenient block-diagonal structure with a common polyad quantum number for each block.[26] We can summarize that the VPT2 approach is a simple, efficient, and economic technique for semi-rigid molecules containing up to 30-40 atoms and even more.[27–30] VPT2 is implemented in some popular quantum-mechanical packages as the default "black-box" method for evaluation of anharmonic energy levels.[5] In addition, VPT2 is capable of evaluating infrared and Raman intensities and some other types of spectra such as VCD.[31–40]

One of the major problems associated with VPT2 is the proper choice and treatment of vibrational resonances that manifest themselves both in the first order (Fermi resonances and associated W-constants) and in the second order (Darling-Dennison resonances, K-constants). This two-step approach was called VPT2+WK in the recent work of Rosnik and Polik.[20] We will follow this terminology. A recent work by Bloino *et al.*[41] presents a good review of the subject and introduces a degeneracy-corrected second-order perturbation theory (DCPT2) and some of its modifications, such as hybrid DCPT2. That work is partly based on an earlier related work[42] that suggested a scheme of algebraic removal of the resonance singularities from expressions for anharmonic constants. The motivation of such studies is dual: VPT2+*WK* must work in an automated mode for large molecules and must ensure smooth variation of frequencies for reaction path studies. However, this approach introduces some approximations and may not serve as a general solution of the resonance problem.

At a glance, one might think that Darling-Dennison resonances are less important than Fermi ones. In fact, one specific type of Darling-Dennison resonance (1-1, see below) directly affects fundamental levels, and such effects can be strong.[30] This resonance also manifests itself in expressions for the vibration-rotation interaction constants α_r^B and is called Coriolis resonance in this context.[11] In addition, Darling-Dennison resonances can cause substantial indirect effect on fundamental levels if, for example, a fundamental level is in a strong Fermi resonance with an overtone and that overtone, in turn, is in strong Darling-Dennison resonance with another overtone. In addition, coupled states participate in substantial intensity redistribution; this effect can cause changes in vibrational intensities by orders of magnitude.

There is one fundamental and underappreciated complication associated with the VPT2 analytic formulas for Darling-Dennison constants K_{DD}. They were originally derived for a resonance-free case and further modified "post-factum" to account for Fermi resonance effects. As we will show below, this approach can fail in certain cases and the underlying theory must be reconsidered.

The first-order Femi resonances manifest themselves by the appearance of near-singular terms with the so-called "resonance denominators" of two types ($(2\omega_r - \omega_s)^{-1}$ and $(\omega_r - \omega_s - \omega_t)^{-1}$) in formulas for anharmonic constants x_{rs} and Darling-Dennison constants K_{DD}. The influence of Fermi resonances on anharmonic constants can be accounted for by manual removal of terms with such resonance denominators and a simultaneous numerical diagonalization of a block of the Hamiltonian matrix in the framework of a post-VPT2 variational "-*WK*" procedure.[11–13,43–45] The influence of the first-order resonances on K_{DD} can also be accounted for by a removal of near-singular terms.[17,20,46,47] The question is whether this procedure is fully justified theoretically. One of the main goals of this paper is providing a comprehensive answer.

What is most important is that in all existing publications the derivations do not explicitly consider the effect of the first-order Fermi resonances on the form of Darling-Dennison resonances from the very beginning. Instead, the traces of them are accounted for "post-factum," without proper consideration of the complex superposition effect of transforming the Hamiltonian in the presence of Fermi resonances. Current work presents a systematic study of the second-order Darling-Dennison resonances using the apparatus of the operator form of canonical Van Vleck perturbation theory (CVPT) and leads to a general method for the correct evaluation of Darling-Dennison resonance constants.

Originally, the first literature description of the second-order resonance appeared in 1940 in Darling and Dennison's paper on the infrared spectrum of H_2O.[48] It was discovered that overtones of two O–H fundamentals were in resonance, and therefore a good fit of a Dunham-type effective Hamiltonian to observed overtones $2\nu_1$ and $2\nu_3$ was impossible. The class of second-order resonances is wider, and the term "Darling-Dennison resonance" can be applied to six other types, namely, 1-1, 2-11, 11-11, 1-3, 1-21, and 1-111 (the dashed sign separates the total number of quanta of excitation and relaxation). The values of resonance coupling coefficients can be calculated using perturbation theory techniques in matrix form (Rayleigh–Schrödinger perturbation theory, RSPT) or in operator form (Canonical Van Vleck perturbation theory, CVPT).[16–20,49] The expressions for 1-111, 1-21, and 1-3 resonances first appeared in the literature in 1997 in Martin and Taylor's paper with some misprints.[17] A recent comprehensive paper by Rosnik and Polik provided a derivation and correct expressions for all types of K_{DD} constants.[20] It is a striking fact that some aspects of the evaluation of the Darling-Dennison constants are still under theoretical scrutiny, after 75 years since their discovery.

Part of the treatment of resonances involves making decisions each time when a suspicious case appears. Does a potential coupling term indeed present a resonance or not? In this connection Fermi resonances are handled quite well. There is one classic work of Martin *et al.*[45] that gives a recipe for detecting both types of Fermi resonances on the grounds of the difference between perturbative or variational accounting for the contributions of cubic force constants φ_{rrs} and φ_{rst} to energy levels. We will analyze this approach in detail below and will show that Martin's resonance criterion can be modified in such a way that it transforms to an approximate linear dependence $f(x) \approx x$, where x is an acceptable error in the calculation and $f(x)$ is the value of the resonance criterion. We will also consider another more general Fermi resonance criterion, which is applicable to Darling-Dennison resonances. The existing methods of detecting Darling-Dennison resonances have an empirical element and are based on consideration of the values of resonance denominators, the ratio of the coupling coefficient to the difference in energy levels (we shall denote it as the Greek letter Ρ), and values of K_{DD} themselves.[20,38,40] We will show that in the framework of the CVPT operator treatment, resonances of any type and at any order can be treated universally.

There is one aspect of the subtle connection between the manifestation of certain resonances and the polyad quantum number to be considered.[21–26] The dimension of the vector space spanned by resonance vectors, composed of the powers of creation and annihilation quanta for vibrational modes M, is typically equal to $M - 1$.[21,26] This rule holds very well for the majority of small molecules (up to ~6 atoms). This restriction helps us decide whether a weak resonance should be considered as a perturbation or a true resonance. However, a full consideration of the connection between resonances and polyads lies beyond the topic of this article because it requires an expert knowledge and deep analysis in each particular case, while we are mostly focused on a general picture and the automation of calculations.

II. PERTURBATION THEORY AND ANHARMONIC RESONANCES

A. Canonical transformations of the Hamiltonian in the absence of resonances

Before proceeding to describe the analysis of main subjects constituting the present study, we remind the reader of the necessary prerequisites of VPT2, such as the choice of coordinates, the form of the Hamiltonian and the method of solution of the Schrödinger equation.

In order to find a system of vibrational energy levels of a molecule, it is necessary to solve a quantum-mechanical Schrödinger equation, which, in turn, is based on a particular choice of internal coordinates and the form of the kinetic and potential energy operators. It is convenient to work with the rectilinear dimensionless normal coordinates $q_r = (4\pi^2 c^2 \omega_r (hc)^{-1})^{1/2} Q_r$, where ω_r is a harmonic frequency, Q_r is a Wilson normal coordinate, and with a conjugate momentum $p_r = -(-1)^{1/2}(\partial/\partial q_r)$ and employ a Watson vibrational Hamiltonian for a non-rotating molecule (the rotational quantum number $J = 0$),[13]

$$H = T + V = \left[\frac{1}{2}\sum_r \omega_r\left(p_r^2 + q_r^2\right)\right] + \left[\frac{1}{6}\sum_{rst}\phi_{rst} q_r q_s q_t\right] + \left[\frac{1}{24}\sum_{rstu}\phi_{rstu} q_r q_s q_t q_u + \sum_{\alpha=x,y,z} B_e^{\alpha}\left(\sum_{r\neq s}\sum_{t\neq u}\zeta_{rs}^{\alpha}\zeta_{tu}^{\alpha}\left(\frac{\omega_s}{\omega_r}\right)^{1/2}\left(\frac{\omega_u}{\omega_t}\right)^{1/2} q_r p_s q_t p_u\right)\right]. \tag{1}$$

Here the terms of the Hamiltonian are grouped by the orders of VPT2. We limit our consideration to asymmetric tops to simplify the formalism. The values of molecular constants B_e^{α}, ζ_{rs}^{α}, ω_r (rotational constants, zeta-constants for Coriolis coupling and harmonic frequencies) appearing in the Hamiltonian from Eq. (1) can be found from the equilibrium molecular structure and harmonic force field, while the cubic and quartic force constants ϕ_{rst} and ϕ_{rstu} can be found using numerical differentiation techniques.[50,51]

The solution of the Schrödinger equation to obtain the energy levels of the Hamiltonian from Eq. (1) can be accomplished using different strategies, of which the variational method and perturbation theory are the most important ones. In our previous publications[49,52,53,30] and in the present study, the Canonical Van Vleck Perturbation Theory (CVPT) is our method of choice because of its generality and convenience.

CVPT preserves the operator representation of the Hamiltonian throughout the canonical transformations that reduce the Hamiltonian to the desired quasi-diagonal form, order by order.[54–59,49] Although the solution can be extended to higher orders (fourth, etc.),[57,49] we confine the present study to the second order. We are mainly interested in a reconsideration and "fine-tuning" of the approach based on analytic formulas, called the VPT2, using a general and powerful numerical-analytic reference implementation of CVPT in the second order, CVPT2. As we indicated in the Introduction, our principal aim is to obtain the correct form for the second-order off-diagonal resonance coupling coefficients.

First, let us consider the form of the once- and twice-transformed Hamiltonian and analyze how vibrational resonances affect the transformations. The general expression below defines the form of the kth-order part of the Hamiltonian, subjected to the Kth canonical transformation,[59–61]

$$\tilde{H}_k^{(K)} = \tilde{H}_k^{(K-1)} + \sum_{j=0}^{n-1}\frac{i^{n-j}}{(n-j)!}\underbrace{\left[S_K,\left[S_K,\ldots\left[S_K,\tilde{H}_{K\times j+m}^{(K-1)}\right]\right]\ldots\right]}_{n-j}, \tag{2}$$

where $i = (-1)^{1/2}$, $n = (k - m)/K$, and $m = \mathrm{mod}(k, K)$ is the remainder of the division of k by K. The transformation operators S_K play the key role in the canonical transformations; they are defined at each order of CVPT in such a way that unwanted off-diagonal terms are cancelled after summation of all parts of the Hamiltonian.

So far, it was implicitly assumed that the whole solution of the Schrödinger equation is accomplished in the coordinate and conjugate momentum representation (see Eq. (1)). At this stage it is worthwhile to remind the reader that although this classical representation was exclusively used in many early studies on VPT2 and CVPT2, it is fundamentally easier to employ a mathematically equivalent representation, based on creation and annihilation operators ($a^{\dagger}$, a), further abbreviated as CAO.[55,58] Then, the Hamiltonian from Eq. (1) is re-expressed through CAO using the following definitions:

$$a^{\dagger} = \frac{1}{\sqrt{2}}(q - i\,p), \quad a = \frac{1}{\sqrt{2}}(q + i\,p), \tag{3}$$

$$q = \frac{1}{\sqrt{2}}(a^{\dagger} + a), \quad p = \frac{1}{\sqrt{2}} i\,(a^{\dagger} - a). \tag{4}$$

In addition, it is convenient to use an associated number operator $\hat{N}$, defined as follows:

$$\hat{N} = a^{\dagger}a, \quad \hat{N}^{[n]} = (a^{\dagger})^n (a)^n. \tag{5}$$

For the following consideration, it is important to introduce the concept of the normal form of CAO.[62] An arbitrary multiple product of CAO can be reduced to an equivalent representation of the form $(a^{\dagger})^{m}(a)^{n}$, where m, n are non-negative integers.

Birss and Choi[55] showed that it is efficient to employ a CAO-representation throughout the whole CVPT treatment, especially because derivation of transformation operators S_K becomes simple in a new formulation. In particular, for obtaining the correct form of operator S_K that is required for cancellation of the following sum of off-diagonal Hamiltonian terms (where χ_j are scalar multipliers),

$$H = \sum_{j} \chi_j \prod_{k=1}^{M} (a_k^{\dagger})^{m_{kj}} (a_k)^{n_{kj}}, \quad m_{kj} \neq n_{kj}, \tag{6}$$

it is sufficient to multiply each term in Eq. (6) by $-i = -(-1)^{1/2}$ and an inverse linear combination, composed of harmonic frequencies taken with integer number weights, equal to powers m_{kj}, n_{kj}, positive for a creation operator and negative for an annihilation operator,[55]

$$S_K = -i \sum_{j} \chi_j \left(\sum_{k=1}^{M} (m_{jk} - n_{jk}) \omega_k \right)^{-1} \prod_{k=1}^{M} (a_k^{\dagger})^{m_{jk}} (a_k)^{n_{jk}}. \tag{7}$$

The commutators $[S, \tilde{H}]$ in Eq. (2) can be evaluated by reducing the products S_K and $\tilde{H}$ to the normal form through the following equality:[57,49]

$$\begin{aligned} &(a^{\dagger})^{k} a^{l} (a^{\dagger})^{m} (a)^{n} \\ &\quad = (a^{\dagger})^{k+m} (a)^{l+n} \\ &\qquad + \sum_{j=1}^{\min(l,m)} \left[\left(\frac{1}{j!} \prod_{i=0}^{j-1} (l-i)(m-i) \right) (a^{\dagger})^{k+m-j} (a)^{l+n-j} \right], \end{aligned} \tag{8}$$

where k, l, m, n are arbitrary non-negative powers of CAO. It is also very convenient to describe vibrational resonances in terms of CAO, as it will be discussed below.

Let us return to the general scheme of CVPT. Applying the Eq. (2), we obtain the following form of the canonically once transformed Hamiltonian,

$$\tilde{H}_0^{(1)} = H_0, \tag{9a}$$

$$\tilde{H}_1^{(1)} = H_1 + i[S_1, H_0], \tag{9b}$$

$$\tilde{H}_2^{(1)} = H_2 + i\,[S_1, H_1] - \tfrac{1}{2}\left[S_1, [S_1, H_0]\right], \tag{9c}$$

In the absence of resonance terms in H_1, the corresponding term $\tilde{H}_1^{(1)}$ can be nullified by the proper choice of operator S_1. This circumstance allows simplifying the form of the term $\tilde{H}_2^{(1)}$ as the double nested commutator can be replaced using[13]

$$H_1^{(1)} = 0 \to 0 = H_1 + i[S_1, H_0] \to [S_1, H_0] = i\,H_1. \tag{10}$$

Therefore, the $\tilde{H}_2^{(1)}$ gains a more tractable form,

$$\tilde{H}_2^{(1)} = H_2 + \tfrac{1}{2} i\,[S_1, H_1]. \tag{11}$$

The summation of terms yields the following formula,[13]

$$\tilde{H}^{(1)} = H_0 + H_2 + \tfrac{1}{2} i\,[S_1, H_1]. \tag{12}$$

which still has some off-diagonal second-order terms. They can be nullified by the second canonical transformation (bearing in mind that the zero- and first-order terms in Eqs. (9a) and (9b) are not affected by it) through using the expression

$$\tilde{H}_2^{(2)} = \tilde{H}_2^{(1)} + i\,[S_2, H_0]. \tag{13}$$

The crucial point is that it is not necessary to consider the second canonical transformation explicitly for the reason that it does not modify the diagonal terms that are responsible for the energy spectrum.[56] The second transformation simply removes all the remaining off-diagonal terms [see Eq. (13)] and affects only the higher-order terms,

$$\tilde{H}_3^{(2)} = \tilde{H}_3^{(1)} + i\left[S_2, \tilde{H}_1^{(1)}\right], \tag{14}$$

$$\tilde{H}_4^{(2)} = \tilde{H}_4^{(1)} + i\left[S_2, \tilde{H}_2^{(1)}\right] - \tfrac{1}{2}[S_2, [S_2, H_0]]. \tag{15}$$

The irrelevance of S_2 for finding the eigenspectrum of $\tilde{H}^{(2)}$ is a reflection of the general rule known as the Wigner theorem: "the block-diagonal part of the K-times transformed Hamiltonian coincides with the effective Hamiltonian up to order $2K + 1$."[56]

The explicit form of S_2 is needed for canonical transformations of the dipole moment operator and other molecular properties such as polarizability, etc.[31–40] However, at this stage our study is focused on the energy spectrum, as it defines the positions of the vibrational bands. In order to obtain the form of the energy expression as a function of vibrational quantum numbers, it is sufficient to evaluate the diagonal matrix elements of $\tilde{H}^{(1)}$,

$$\begin{aligned} \langle \Psi_A(\bar{\upsilon}) | \tilde{H}^{(1)} | \Psi_A(\bar{\upsilon}) \rangle &= \langle \Psi_A(\bar{\upsilon}) | H_0 + H_2 \\ &\quad + \tfrac{1}{2} i\,[S_1, H_1] | \Psi_A(\bar{\upsilon}) \rangle. \end{aligned} \tag{16}$$

The resulting expression is a familiar form of the Dunham-type energy expansion as a function of vibrational quantum numbers υ_r and spectroscopic constants G_0, ω_r, and x_{rs},[13]

$$\begin{aligned} E(hc)^{-1} &= G_0 + \sum_{r}^{M} \omega_r \left(\upsilon_r + \frac{1}{2} \right) \\ &\quad + \sum_{r \le s}^{M} x_{rs} \left(\upsilon_r + \frac{1}{2} \right) \left(\upsilon_s + \frac{1}{2} \right). \end{aligned} \tag{17}$$

The off-diagonal matrix elements of $\tilde{H}^{(1)}$ are not necessarily nil. At this stage we consider a resonance-free case; hence we can regard all off-diagonal couplings as irrelevant on the grounds that they should have been explicitly eliminated by S_2, if necessary.

B. Canonical transformations of the Hamiltonian in the presence of resonances

So far we were considering an idealized resonance-free situation. However, resonance effects are universally present in molecular dynamics. It is well known that the perturbation treatment of resonance interactions usually leads to abnormally large values of anharmonic constants and poor fits of Dunham's energy expression to observed values. The treatment of resonances was discussed in the early papers of Nielsen[9,10,63] and in numerous subsequent publications of different authors. The general method consists in separation of resonance terms from the perturbation treatment and the numerical diagonalization.

We will show below that the standard method of dealing with the second-order resonances is not strict with regard to evaluation of Darling-Dennison constants. In brief, usually the effect of the Fermi resonances on anharmonic constants is dealt by removing the terms with so-called "resonance denominators."[44,45] The similar treatment of first-order resonance effects in the expressions for the second-order Darling-Dennison resonances has been also discussed in the literature.[17,46,47] However, it is not evident if the values of Darling-Dennison constants obtained by the aforementioned semi-empirical procedure of removal of the first-order resonance terms coincide with the exact values. The term "exact value" in this context relates to the possibility of carrying out two canonical transformations explicitly in the framework of the CVPT procedure, while maintaining an analytic operator representation of the original and transformed Hamiltonian at all stages until the final integration and determination of matrix elements.[57,49] It is therefore worthwhile to reconsider the general formalism from the very beginning to highlight the essence of the problem.

The general equations for the first canonical transformations in Eqs. (9a)–(9c) do not change significantly in the case when the first- and/or second-order terms of the original Hamiltonian are partly resonant. Equation (9b) can be rewritten as follows:

$$H_1^{(1)} = H_1 + i[S_1^*, H_0] = (H_1^* + H_1^\dagger) + i[S_1^*, H_0]. \tag{18}$$

Here we introduce a new notation that is based on partitioning the term H_1 into purely non-resonant (*) and purely resonant (†) parts, $H_1 = H_1^* + H_1^\dagger$. Consequently, the canonical transformation generator now only affects the non-resonant terms; it is denoted S_1^*. Now, only the non-resonant terms of the Hamiltonian are cancelled, and the Eq. (10) gains a new form,

$$\begin{aligned} H_1^{(1)} = H_1^\dagger \rightarrow H_1^\dagger &= (H_1^* + H_1^\dagger) + i[S_1^*, H_0] \\ &\rightarrow [S_1^*, H_0] = i\, H_1^*. \end{aligned} \tag{19}$$

The modified generator S_1^* must be further applied to higher-order perturbations of the Hamiltonian, and the second-order term gains the following form, analogous to Eq. (9c):

$$\begin{aligned} \tilde{H}_2^{(1)} &= H_2 + i[S_1^*, H_1] - \tfrac{1}{2}\, [S_1^*, [S_1^*, H_0]] \\ &= H_2 + i[S_1^*, (H_1^* + H_1^\dagger)] - \tfrac{1}{2} i\, [S_1^*, H_1^*] \\ &= H_2 + \tfrac{1}{2} i\, [S_1^*, H_1^*] + i[S_1^*, H_1^\dagger]. \end{aligned} \tag{20}$$

After summation of all orders up to the second, we obtain the final expression

$$\begin{aligned} H^{(1)} &= H_0 + H_1^\dagger + H_2 + \tfrac{1}{2} i\, [S_1^*, H_1^*] + i[S_1^*, H_1^\dagger] \\ &= H_0 + H_1^\dagger + H_2 + \tfrac{1}{2} i\, [S_1^*, (H_1^* + 2H_1^\dagger)]. \end{aligned} \tag{21}$$

This expression is the main one for obtaining both diagonal and off-diagonal matrix elements; it properly accounts for the first-order resonances. By comparing this expression with the non-resonant one (Eq. (12)), we see that they are different. First, there is the first-order unmodified term $H_1^\dagger$ that makes no direct contribution to diagonal matrix elements but creates a small number of off-diagonal terms responsible for Fermi resonances, which are further treated by a matrix diagonalization. Second, the commutator $\frac{1}{2} i\, [S_1, H_1]$ transforms into $\frac{1}{2} i\, [S_1^*, (H_1^* + 2H_1^\dagger)]$. This difference requires further careful consideration.

It is essential to remember that at the stage of derivation of the closed-form expressions it is difficult to discriminate the resonant parts from the non-resonant ones because the difference depends on particular values of Hamiltonian constants. The difficulty of this discrimination is the key point of the whole problem. In order to compare the "pure" and "resonant" forms of $H^{(1)}$ and to reveal the crucial point of our study, let us return to the original resonance-free, Eqs. (9) and (10), and separate the generator S_1 into two parts, $S_1^* + S_1^\dagger$, the first one must remain in the correct resonance-free treatment and the second one is redundant and must be somehow eliminated from the final expressions. Considering the key commutator $\frac{1}{2} i [S_1, H_1]$ in Eq. (10), we therefore obtain

$$\begin{aligned} \tfrac{1}{2} i [S_1, H_1] &= \tfrac{1}{2} i\, [(S_1^* + S_1^\dagger), (H_1^* + H_1^\dagger)] \\ &= \tfrac{1}{2} i\, [S_1^*, (H_1^* + 2H_1^\dagger)] - \tfrac{1}{2} i [S_1^*, H_1^\dagger] \\ &\quad + \tfrac{1}{2} i\, [S_1^\dagger, H_1]. \end{aligned} \tag{22}$$

Substitution of this commutator into Eq. (10) and comparing the result with the correct form of Eq. (21) shows that the last two terms in Eq. (22) are redundant and must be removed in the framework of a certain systematic procedure. The "usual" expression (Eq. (10)) does not assume the presence of resonant terms, and the term H_1 is also not separated into resonant and non-resonant parts. Now, we have to understand how to deal with two last commutators in Eq. (22).

Fortunately, the last commutator in Eq. (22), $\frac{1}{2} i\, [S_1^\dagger, H_1]$, which contributes to both diagonal and off-diagonal matrix elements, has a distinct "signature," which is the presence of well known "resonance denominators." Such terms can be manually eliminated, and this procedure for their removal is a justification of the standard method of dealing with resonances for both anharmonic constants and Darling-Dennison ones.[11–13,17,44–47,20] It can be easily proven that the terms, related to the commutator $\frac{1}{2}i\ [S_1^\dagger, H_1]$, are characterized by the presence of the resonance denominators of the kind $(\pm 2\omega_i \pm \omega_j)^{-1}$ and $(\pm\omega_i \pm \omega_j \pm \omega_k)^{-1}$, where certain combinations of harmonic frequencies must be necessarily related to recognized Fermi resonances.[11–13]

The remaining commutator $-\frac{1}{2}i[S_1^*, H_1^\dagger]$ in Eq. (22) is also redundant, but it has no special features. Thus, we must study it properties separately. This commutator is generally not nil and consists of the off-diagonal operators with a total power equal to two or four which do not affect diagonal anharmonic constants. The crucial point of our study is finding out whether this commutator affects the values of Darling-Dennison constants. There are no evident prerequisites that can ensure that this commutator cannot contribute to the second-order off-diagonal matrix elements. We will not reveal a final answer until Sec. III C but can say that we have found the answer using numerical experiments for particular molecules.

To conclude this section, we summarize that the correct expression for the anharmonic constants and Darling-Dennison constants can be obtained as the following diagonal and off-diagonal matrix elements, respectively,

$$\begin{aligned}&\langle\Psi_A(\bar{v})|H^{(1)}|\Psi_A(\bar{v})\rangle\\ &\quad= \langle\Psi_A(\bar{v})|H_0 + H_2 + \tfrac{1}{2}i\ [S_1^*, H_1^*]|\Psi_A(\bar{v})\rangle,\end{aligned} \tag{23}$$

$$\begin{aligned}&\langle\Psi_A(\bar{v})|H^{(1)}|\Psi_B(\bar{v})\rangle\\ &\quad q = \langle\Psi_A(\bar{v})|H_2 + \tfrac{1}{2}i\ [S_1^*, H_1^*] + i[S_1^*, H_1^\dagger]|\Psi_B(\bar{v})\rangle.\end{aligned} \tag{24}$$

Before we conclude this Section, we remind the reader that it is convenient to express any resonance using CAO. The operator $\hat{F} = H_1^\dagger + H_2^\dagger$, representing the off-diagonal part of the Hamiltonian after two canonical transformations, has the following general form:

$$\begin{aligned}&\hat{F} = \sum_j \left[F_j \prod_{k=1}^{M} ((a_{jk}^\dagger)^{m_{jk}}(a_{jk})^{n_{jk}} + (a_{jk})^{m_{jk}}(a_{jk}^\dagger)^{n_{jk}})\right],\\ &m_{jk} \neq n_{jk}, \quad \sum_{k=1}^{M} m_{jk}\omega_k \approx \sum_{k=1}^{M} n_{jk}\omega_k.\end{aligned} \tag{25}$$

As we mentioned above, it is not necessary to consider the second canonical transformation explicitly, since small off-diagonal terms, originating from H_2, do not contribute to the diagonal matrix elements in second order.

Individual terms in the resonance operator $\hat{F}$ of Eq. (25) can be classified by the total power of CAO into two categories: odd or even. Fermi resonances of types 1-2 and 1-11 are associated with operators of the following kind with odd CAO powers,

$$\hat{F}_{i,jj}^{(1)} = F_{i,jj}(a_i^\dagger)(a_j)^2, \quad \hat{F}_{i,jk}^{(1)} = F_{i,jk}(a_i^\dagger)(a_j)(a_k). \tag{26}$$

Darling-Dennison resonances of types 1-1, 2-2, 2-11, 11-11, 1-3, 1-21, 1-111 appear at the second order of canonical transformations, and the corresponding operators have a similar form as Eq. (26). Of them, the 1-1 resonance is represented by three types of operators,

$$\begin{aligned}&\hat{F}_{i,j}^{(2)} = V_{i,j}(a_i^\dagger)(a_j), \quad \hat{F}_{ii,ij}^{(2)} = V_{ii,ij}(a_i^\dagger)\hat{N}_i(a_j),\\ &\hat{F}_{ij,jk}^{(2)} = V_{ij,jk}(a_i^\dagger)\hat{N}_j(a_k),\end{aligned} \tag{27}$$

and will be considered in detail below.

C. The systematic choice of the first-order resonance criteria

In the previous section we have seen that the first-order Fermi resonances directly affect the Darling-Dennison resonances. Therefore, it is important to introduce a systematic and physically supported approach for the detection of Fermi resonances.

Several kinds of physical quantities can be considered for making a decision about the interaction between states that should be treated as resonance. In the framework of the standard Rayleigh-Schrödinger perturbation theory, a perturbed wave function in the first order can be expressed as a linear combination of the zero-order wave functions, $\Psi_k^{(1)} = \sum_{l\neq k} C_{k,l}^{(1)}\Psi_l^{(0)}$, where the coefficients of the linear combination are matrix elements for off-diagonal coupling divided by the difference in zero-order energy levels, i.e., $C_{k,l}^{(1)} = \frac{\langle\Psi_l^{(0)}|\hat{F}|\Psi_k^{(0)}\rangle}{E_k^{(0)} - E_l^{(0)}}$, where $\hat{F}$ is a perturbation. These ratios define the level of mixing of zero-order states and characterize the applicability of the perturbation theory.

One popular criterion of selecting Fermi resonances was formulated by Martin *et al.*[45] It is based on the estimation of the effect of including or excluding the near-singular interaction in the effective Hamiltonian for a fundamental transition using the 2 × 2 model case. For a Type I Fermi resonance $(2\omega_i \approx \omega_k)$ and for a Type II resonance $(\omega_i + \omega_j \approx \omega_k)$, respectively, these effects $X^{(I)}$, $X^{(II)}$ are given by[45]

$$X^{(I)} = \frac{D_{iik}}{2}\left(\sqrt{1 + \frac{\phi_{iik}^2}{4D_{iik}^2}} - 1 - \frac{\phi_{iik}^2}{8\Delta_{iik}^2}\right), \tag{28}$$

$$X^{(II)} = \frac{D_{ijk}}{2}\left(\sqrt{1 + \frac{\phi_{ijk}^2}{2D_{ijk}^2}} - 1 - \frac{\phi_{ijk}^2}{4\Delta_{ijk}^2}\right). \tag{29}$$

Here the quantities $\Delta(\omega)$ and $D(\nu^*)$, composed of harmonic (ω_i) and anharmonic $(\nu_i^*, (2\nu_i)^*, (\nu_i + \upsilon_j)^*)$ frequencies, have the following meaning (the asterisk denotes deperturbation of the anharmonic constants used for evaluation of fundamentals and the values in brackets are for overtones and combination bands, respectively):

$$\Delta_{iik} = 2\omega_i - \omega_k, \quad \Delta_{ijk} = \omega_i + \omega_j - \omega_k, \tag{30}$$

$$D_{iik} = |(2\nu_i)^* - \nu_k^*|, \quad D_{ijk} = |(\nu_i + \nu_j)^* - \nu_k^*|. \tag{31}$$

If effects $X^{(I)}, X^{(II)}$ exceed a threshold value X^* and the value of resonance denominator is less than a certain threshold value Δ^*, the interaction considered must be treated variationally. The criterion $X^{(I)}, X^{(II)} \geq X^*$ has dimension of cm^{-1} and is usually chosen empirically. For example, in Refs. 38 and 40 choosing $\Delta^* = 200\ \text{cm}^{-1}$ and $X^* = 1\ \text{cm}^{-1}$ was suggested.

Let us consider the criterion used by Martin *et al.*[45] in more detail in order to reveal its strong and weak points. The effect of "deperturbation" of the anharmonic constants by removal of the terms containing denominators $2\omega_i - \omega_k$ (Type I) or $\omega_i + \omega_j - \omega_k$ (Type II) alters the values of the fundamental frequencies ν_k as follows:[45]

$$\nu_k^{(I)} = \nu_k^* - \frac{\phi_{iik}^2}{16\Delta_{iik}}, \quad \nu_k^{(II)} = \nu_k^* - \frac{\phi_{ijk}^2}{8\Delta_{ijk}}. \tag{32}$$

On the other hand, the variational values of ν_k after the diagonalization of the 2×2 matrices

$$\begin{pmatrix} (2\nu_i)^* & \phi_{iik}/4 \\ \phi_{iik}/4 & \nu_k^* \end{pmatrix}, \quad \begin{pmatrix} (\nu_i + \nu_j)^* & \phi_{ijk}/\sqrt{8} \\ \phi_{ijk}/\sqrt{8} & \nu_k^* \end{pmatrix} \tag{33}$$

have the following roots (assuming that $(2\nu_i)^* > \nu_k^*$ and $(\nu_i + \nu_j)^* > \nu_k^*$):

$$\nu_{\pm}^{(I)} = \left(\nu_k^* + \frac{D_{iik}}{2}\right) \pm \frac{D_{iik}}{2}\sqrt{1 + \frac{\phi_{iik}^2}{4D_{iik}^2}}, \tag{34}$$

$$\nu_{\pm}^{(II)} = \left(\nu_k^* + \frac{D_{ijk}}{2}\right) \pm \frac{D_{ijk}}{2}\sqrt{1 + \frac{\phi_{ijk}^2}{2D_{ijk}^2}}. \tag{35}$$

Choosing the correct signs in Eqs. (34) and (35) on the assumption that $2\omega_i > \omega_k$ and $\omega_i + \omega_j > \omega_k$, we obtain, after subtracting Eqs. (34) and (35) from Eq. (32),

$$\begin{aligned} \nu_k^{(I)} - \nu_-^{(I)} &= -\frac{\phi_{iik}^2}{16\Delta_{iik}} - \frac{D_{iik}}{2} + \frac{D_{iik}}{2}\sqrt{1 + \frac{\phi_{iik}^2}{4D_{iik}^2}} \\ &= -\frac{\phi_{iik}^2}{16\Delta_{iik}} + \frac{D_{iik}}{2}\left(\sqrt{1 + \frac{\phi_{iik}^2}{4D_{iik}^2}} - 1\right), \end{aligned} \tag{36}$$

$$\begin{aligned} \nu_k^{(II)} - \nu_-^{(II)} &= -\frac{\phi_{ijk}^2}{8\Delta_{ijk}} - \frac{D_{ijk}}{2} + \frac{D_{ijk}}{2}\sqrt{1 + \frac{\phi_{ijk}^2}{2D_{ijk}^2}} \\ &= -\frac{\phi_{ijk}^2}{8\Delta_{ijk}} + \frac{D_{ijk}}{2}\left(\sqrt{1 + \frac{\phi_{ijk}^2}{2D_{ijk}^2}} - 1\right). \end{aligned} \tag{37}$$

These expressions coincide with Eqs. (A24) and (A25) from Ref. 45 if we accept that $\Delta(\omega) \approx D(\nu^*)$. Since the quantities $D(\nu^*)$ are unknown at the stage of selecting Fermi resonances, there is no other alternative.

Martin *et al.*[45] further simplified the quantities $X^{(I)}$ and $X^{(II)}$ (Eqs. (28) and (29)) by taking the major part of the following expansion in a Taylor series:

$$f(x) = a\left(\sqrt{1+x} - 1 - \frac{1}{2}x\right) \approx -\frac{1}{8}a\,x^2 + \frac{1}{16}a\,x^3 + \ldots. \tag{38}$$

Assuming $X^{(I)}$ and $X^{(II)}$ be functions of variables $\frac{\phi_{iik}^2}{4D_{iik}^2}$ and $\frac{\phi_{ijk}^2}{2D_{ijk}^2}$, and assuming $\Delta(\omega) \approx D(\nu^*)$, we obtain the following simplification of Eqs. (28) and (29) using (38):

$$X^{(I)} = \frac{D_{iik}}{2}\left(\sqrt{1 + \frac{\phi_{iik}^2}{4D_{iik}^2}} - 1 - \frac{\phi_{iik}^2}{8\Delta_{iik}^2}\right) \approx -\frac{\phi_{iik}^4}{256\Delta_{iik}^3}, \tag{39}$$

$$X^{(II)} = \frac{D_{ijk}}{2}\left(\sqrt{1 + \frac{\phi_{ijk}^2}{2D_{ijk}^2}} - 1 - \frac{\phi_{ijk}^2}{4\Delta_{ijk}^2}\right) \approx -\frac{\phi_{ijk}^4}{64\Delta_{ijk}^3}. \tag{40}$$

A more general approach can be formulated on the basis of direct consideration of the Canonical Van Vleck Perturbation Theory in operator form. CVPT works well unless the dimensionless scalar coefficients Ξ_l of S_K operators exceed a certain threshold value Ξ^*. These coefficients Ξ_l have a simple structure (see Eq. (7)) as a Hamiltonian coefficient χ_l (proportional to a force constant in case of S_1 or more complex expressions in higher orders) divided by a linear combination of zero-order frequencies, such as $\Delta_{iik} = 2\omega_i - \omega_k$ or $\Delta_{ijk} = \omega_i + \omega_j - \omega_k$ in case of Fermi resonances (Types I and II).

It is easy to obtain explicit expressions for coefficients $\Xi_l^{(I)}$, $\Xi_l^{(II)}$ directly from the corresponding cubic terms of the Hamiltonian. The force constant ϕ_{iik} has a factorial multiplier of 1/3! and a combinatorial multiplicity factor of 3, producing the net coefficient 1/2. Converting each power of a normal coordinate into a CAO representation introduces a multiplier $2^{-1/2}$ (see Eq. (4)). In total, the 1-2 Fermi resonance operator coefficient becomes $(2^{1/2}/8)\phi_{iik}$. For the 1-11 Fermi resonance operator coefficient we similarly obtain (the multiplicity factor = 6) the value of operator coefficient $8^{-1/2}\phi_{ijk}$. Dividing these operator coefficients by the Δ_{iik} and Δ_{ijk}, we obtain the following resonance conditions:

$$\begin{aligned} \Xi_l^{(I)} &= \frac{1}{2\sqrt{8}}\left|\frac{\phi_{iik}}{2\omega_i - \omega_k}\right| > \Xi^*, \\ \Xi_l^{(II)} &= \frac{1}{\sqrt{8}}\left|\frac{\phi_{ijk}}{\omega_i + \omega_j - \omega_k}\right| > \Xi^*. \end{aligned} \tag{41}$$

In higher orders, the coefficients Ξ_l have a similar form as a ratio of a more complex coefficient, divided by a linear combination of harmonic frequencies, as can be seen from Eq. (7). The dimensionless quantity Ξ_l can be called the *resonance index*.[49,52] Essentially the same quantities as Eq. (41) were empirically introduced in Refs. 64 and 65 for detecting Fermi resonances, but without numerical coefficients, and the cut-off value was chosen as 0.20.

There are many empirical ways to judge if certain levels are strongly coupled and should be treated as resonant. For example, fitting resonant spectroscopic terms by variation of anharmonic constants in the Dunham-type expansion will result in an abnormal residual discrepancy. Darling and Dennison discovered the 2-2 resonance in water molecule in this way.[48] In addition, resonating groups of levels cause a significant redistribution of line intensities. There are many well-studied cases of resonance effects in small molecules. By studying typical values of quantities Ξ_l for small molecules, it can be found that the value of resonance index threshold Ξ^* typically lies in the region 0.05-0.50 (unitless). Concerning the topic of this paper, the biggest advantage of using the resonance index is that it is physically meaningful and universal both for

Fermi resonances and in second order, for Darling-Dennison resonances, which minimizes the dependence on empiricism.

There is one novel method[26] of finding the cutoff value Ξ^* of the resonance index. It is based on consideration of clustering of vibrational states interlinked by multiple resonances. Such clusters are called polyads, and this concept plays a fundamental role in the theory of molecular vibrations and dynamics.[21–25] The Hamiltonian matrix arranged by polyad states with the same value of a polyad quantum number has a block-diagonal structure. It is evident that all interpolyad interactions are non-resonant while within polyads there can be multiple resonance interactions. Many thoroughly studied cases demonstrate this relationship. We have previously shown[26] that the analysis of the polyad structure and determination of the polyad coefficients (which are integer weight coefficients that account for contributions of normal mode quantum numbers into common polyad number) permits finding the cutoff value Ξ^* for resonance interactions confined to polyad blocks.

D. The relationship between resonance operator coefficients and matrix elements

While VPT2 provides analytic expressions for Fermi resonance constants W and Darling-Dennison constants K_{DD}, the CVPT2 implementation yields the resonance operators expressed in creation/annihilation operators (CAO). In our opinion, the calculation of values of matrix elements using the explicit form of resonance operators is a preferred scheme for the final variational stage as it minimizes the risk of errors. To be precise, when dealing with analytic formulas, it is essential to know the location of all matrix elements that are contributing. On the other hand, when an overall effect of all available resonances on a certain matrix element is needed, it is very convenient to take a pair of wave functions, defined by sets of their quantum numbers, and scan all available resonance operators to obtain an exact result,

$$H_{AB} = \langle \bar{v}^{(A)} | \sum_j F_j \prod_{k=1}^{M} (a_k^\dagger)^{m_{kj}} (a_k)^{n_{kj}} | \bar{v}^{(B)} \rangle. \tag{42}$$

Therefore, when dealing with a large number of different kinds of resonances, it is necessary to have handy formulas interconnecting coefficients F of resonance operators and VPT2 constants W, K. A collection of such formulas for all types of Fermi and Darling-Dennison resonances is provided in the supplementary material.[66] The case of the 1-1 Darling-Dennison resonance is most complicated and is given by the following expression:

$$\begin{aligned} H_{r,s}(\bar{v}) &= \langle v_r + 1, v_s | \hat{F}_{r,s} | v_r, v_s + 1 \rangle \\ &= \tfrac{1}{4}\sqrt{(v_r+1)(v_s+1)} \\ &\quad \times \Bigg[3K_{rr,rs}(v_r+1) + 3K_{rs,ss}(v_s+1) \\ &\quad + \sum_{j \neq r,s} 2K_{rj,sj}\left(v_j + \frac{1}{2}\right)\Bigg] \neq 0 \end{aligned}$$

$$\begin{aligned} \rightarrow\ \hat{F}_{r,s} &= H_{r,s}(v_r = 1, v_s = 1)[a_r^\dagger a_s + a_r a_s^\dagger] \\ &\quad + \frac{3}{4}\sum_{k=r,s} K_{rk,sk}[a_r^\dagger a_k^\dagger a_k a_s + a_r a_k^\dagger a_k a_s^\dagger] \\ &\quad + \frac{1}{2}\sum_{k \neq r,s} K_{rk,sk}[a_r^\dagger a_s a_k^\dagger a_k + a_r a_s^\dagger a_k^\dagger a_k]. \end{aligned} \tag{43}$$

E. Special case of Darling-Dennison resonance: 1-1

The 1-1 Darling-Dennison resonance is a special one and its nature is rather unusual and interesting. Unlike any other Fermi or Darling-Dennison resonance, the 1-1 type couples two fundamental levels (they must have the same symmetry). This type of resonance also manifests itself in vibration-rotation coupling constants α_r^B and is often called Coriolis resonance.[11] A classical example of 1-1 resonance is formaldehyde, where ν_2 and ν_3 are coupled by a matrix element $\langle v_{j\neq 2} = 0, v_2 = 1 | \hat{F}_{2,3} | v_{k\neq 3} = 0, v_3 = 1\rangle = 7\ \mathrm{cm}^{-1}$. Recently we observed a strong case of 1-1 resonance in the porphin molecule.[30]

If such a resonance is manifesting itself for a certain molecule, the family of corresponding resonance operators is given by a set of $M+1$ operators,[49]

$$\hat{F}_{rs} = f_0 a_r^\dagger a_s + \sum_{j=1}^{M} f_j a_r^\dagger \hat{N}_j a_s. \tag{44}$$

This is an unusual situation as all the other first- and second-order resonances can be represented by a single-term resonance operator. The reason for this behavior is that a 1-1 resonance can be thought of as "zero-order resonance that manifests itself only in the second order." It should be noted that within a commonly employed vibrational perturbation theory model the zero-order is chosen in such a way that all degrees of freedom are fully separated. Therefore, the absence of the 1-1 resonance at the first order in VPT2 is a consequence of the chosen representation.

It was shown earlier that if a certain resonance first reveals itself in Lth order, then in (L+K)th order its operators are appended with terms multiplied by number operators in (K–L)/2th power.[49,59] Comparing Eq. (44) with the general expression for the Kth order resonance operator,[49,59]

$$\begin{aligned} \hat{F}^{(K)} = \prod_{l=1}^{M} (a_l^\dagger)^{m_l} \Bigg[& f_0^{(K)} + \sum_{j=1}^{M} f_j^{(K)} \hat{N}_j + \ldots \\ & + \sum_{j=1}^{M}\sum_{k=j}^{M} \ldots f_{jk\ldots}^{(K)} \hat{N}_j \hat{N}_k \ldots \Bigg] \prod_{l=1}^{M} (a_l)^{n_l}, \end{aligned} \tag{45}$$

Eq. (44) can be rewritten as follows:

$$\hat{F}_{rs}^{(2)} = a_r^\dagger \left[f_0^{(2)} + \sum_{j=1}^{M} f_j^{(2)} \hat{N}_j \right] a_s. \tag{46}$$

It was shown earlier[49,59] that the general form of the matrix element corresponding to the resonance operator (45) is given by

$$\begin{aligned} \mathrm{X}^{(K)}_{A,B} &= \left\langle \prod_{l=1}^{M} \Psi_0\left(v_l^A\right) \right| \hat{F}^{(K)} \left| \prod_{l=1}^{M} \Psi_0\left(v_l^B\right) \right\rangle \\ &= \left(\prod_{l=1}^{M} C_l^{(m_l)} C_l^{(n_l)} \right) \left[f_0^{(K)} + \sum_{j=1}^{M} f_j^{(K)} v_j + \ldots + \sum_{j=1}^{M} \sum_{k=j}^{M} \ldots f_{jk}^{(K)} v_j v_k \ldots \right], \end{aligned} \tag{47}$$

where (a typographical mistake in Eq. (6.23) of Ref. 49 is corrected here)

$$C_l^{(m_l)} = \prod_{k=1}^{m_l} \sqrt{v_l^A - k + 1}, \quad C_l^{(n_l)} = \prod_{k=1}^{n_l} \sqrt{v_l^B - k + 1}. \tag{48}$$

In the case of the 1-1 second order resonance, the matrix element expression (47) can be rewritten in the following form:

$$\begin{aligned} \mathrm{X}^{(2)}_{A,B} &= \left\langle \prod_{l=1}^{M} \Psi_0\left(v_l^A\right) \right| \hat{F}_K \left| \prod_{l=1}^{M} \Psi_0\left(v_l^B\right) \right\rangle = \left(\prod_{l=1}^{M} C_l^{(m_l)} C_l^{(n_l)} \right) \left[f_0^{(2)} + \sum_{j=1}^{M} f_j^{(2)} v_j \right] \\ &= \left(\prod_{l=1}^{M} C_l^{(m_l)} C_l^{(n_l)} \right) \left[\left(f_0^{(2)} - \frac{1}{2} \sum_{j=1}^{M} f_j^{(2)} \right) + \sum_{j=1}^{M} f_j^{(2)} \left(v_j + \frac{1}{2} \right) \right]. \end{aligned} \tag{49}$$

It is useful to compare this expression with the more standard form of the 1-1 resonance matrix element. Hänninen and Halonen gave the following formula:[18]

$$\begin{aligned} \langle v_r + 1, v_s | \hat{H} | v_r, v_s + 1 \rangle &= \frac{\left[(v_r+1)(v_s+1)\right]^{1/2}}{4} \\ &\times \left[3K_{rr,rs}(v_r+1) + 3K_{rs,ss}(v_s+1) + \sum_{j \neq r,s} 2K_{rj,sj} \left(v_j + \frac{1}{2} \right) \right] = \frac{\left[(v_r+1)(v_s+1)\right]^{1/2}}{4} \\ &\times \left[\left(3(K_{rr,rs} + K_{rs,ss}) + \sum_{j \neq r,s} K_{rj,sj} \right) + 3K_{rr,rs} v_r + 3K_{rs,ss} v_s + 2 \sum_{j \neq r,s} K_{rj,sj} v_j \right]. \end{aligned} \tag{50}$$

The expressions for constants $K_{rr,\,rs}$ and $K_{rj,\,sj}$ are presented in Halonen's work[18] (Eqs. (12) and (13) in Ref. 18). Rosnik and Polik[20] gave separate expressions for $K_{rr,\,rs}$ and $K_{rs,\,ss}$, but it is evident that one of them can be obtained from the other by permutation of indices.

By comparing the expressions in Eqs. (49) and (50), we can see that the traditional equation (50) can be regrouped to match the uniform structure of Eq. (49) where the expression in square brackets is a constant term plus a sum over all degrees of freedom uniformly multiplied by a quantum numbers plus 1/2 (summation here includes indices r and s),

$$\langle v_r + 1, v_s | \tilde{H} | v_r, v_s + 1 \rangle = \frac{\left[(v_r+1)(v_s+1)\right]^{1/2}}{4} \left[\frac{1}{2}(K'_{rr,rs} + K'_{rs,ss}) + \sum_{j=1}^{M} K'_{rj,sj} \left(v_j + \frac{1}{2} \right) \right], \tag{51}$$

where $K'_{rr,\,rs} = 3K_{rr,\,sr}$, $K'_{rs,\,ss} = 3K_{rs,\,ss}$, $K'_{rj,\,sj} = 2K_{rj,\,sj}$. By comparing Eq. (51) with Eq. (49), we obtain the relationships between resonance operator coefficients $f_j^{(2)}$ and constants K',

$$\frac{1}{2}\left(K'_{rr,rs} + K'_{rs,ss}\right) = 4\left(f_0^{(2)} - \frac{1}{2} \sum_{j=1}^{M} f_j^{(2)} \right), \quad K'_{rj,sj} = 4 f_j^{(2)}, \tag{52}$$

$$f_0^{(2)} = \frac{1}{8}\left(K'_{rr,rs} + K'_{rs,ss} + \sum_{j=1}^{M} K'_{rj,sj} \right), \quad f_j^{(2)} = \frac{1}{4} K'_{rj,sj}. \tag{53}$$

It is seen from Eqs. (43) and (51) that it is impossible to separate a unique constant that can be called "Darling-Dennison 1-1 resonance constant $K_{DD}^{(1-1)}$" since it is dependent on quantum numbers. But the constant $f_0^{(2)}$ does possess the necessary property and can be considered in lieu of $K_{DD}^{(1-1)}$. For convenience, we present the expressions for modified constants K',

$$\begin{aligned} K'_{aa,ab} = {} & \frac{1}{2}\phi_{aaab} - \frac{1}{8}\sum_k \phi_{aak}\phi_{abk}\left(\frac{1}{\omega_a+\omega_a+\omega_k} + \frac{1}{-\omega_a-\omega_a+\omega_k} + \frac{4}{\omega_k}\right) \\ & - \frac{1}{8}\sum_k \phi_{aak}\phi_{abk}\left(\frac{1}{\omega_a+\omega_a+\omega_k} + \frac{1}{-\omega_a-\omega_a+\omega_k} + \frac{2}{\omega_a-\omega_a+\omega_k} + \frac{2}{-\omega_a+\omega_a+\omega_k}\right), \end{aligned} \tag{54}$$

$$\begin{aligned} K'_{ac,bc} = {} & \phi_{abcc} + 4\sum_\alpha B_\alpha \zeta_{ac}^{\alpha}\zeta_{bc}^{\alpha}\frac{\omega_a\omega_b+\omega_c^2}{\omega_c\sqrt{\omega_a\omega_b}} \\ & - \frac{1}{4}\sum_k \phi_{kab}\phi_{kcc}\left(\frac{2}{\omega_k} + \frac{1}{\omega_a-\omega_b+\omega_k} + \frac{1}{\omega_b-\omega_a+\omega_k}\right) \\ & - \frac{1}{4}\sum_k \phi_{kac}\phi_{kbc}\left(\frac{1}{\omega_a+\omega_b+\omega_k} + \frac{1}{\omega_b-\omega_a+\omega_k} + \frac{1}{\omega_a-\omega_b+\omega_k} + \frac{1}{\omega_k-\omega_a-\omega_b}\right). \end{aligned} \tag{55}$$

A comprehensive derivation of expressions for all types of Darling-Dennison resonance coupling constants was accomplished in a recent fine study of Rosnik and Polik.[20] They employed a matrix form of the canonical Van Vleck perturbation theory and coordinate-conjugated momenta (q, p) representation. The starting point of their study was a quartic Watson Hamiltonian (1). Then, a sequence of matrix transformations was applied, that cancelled off-diagonal Hamiltonian terms, subdivided into two classes, the weakly and strongly interacting states, respectively. The order of transformations and terminology is somewhat different from the standard treatment of Papousek and Aliev,[13] but the final results for all K_{DD} constants are correct, to the best of our knowledge. However, even the extraordinary thorough and accurate paper of Rosnik and Polik[20] is not free of errors as we shall see below in the section concerning the zero-point vibrational energy.

F. Anharmonic zero-point vibrational energy (ZPVE)

Quantum chemistry permits finding an electronic energy minimum of a molecule, and approximating the potential energy surface by a grid of points or the expansion coefficients of a Taylor series. The system of quantized vibrational levels is usually found through an independent solution of the vibrational Schrödinger equation. The zero-point vibrational energy (ZPVE or E_0), corresponding to the lowest vibrational quantum state, is an essential parameter for calculation of thermodynamic functions, such as an internal energy. An accurate calculation of the anharmonic quantum mechanical vibrational partition function, Q_{vib}, that is a function of E_0, is necessary for the theoretical prediction of thermodynamic functions and equilibrium constants. For instance, in applications of chemical reaction transition state theory, the values of Q_{vib} are required both for the reactants and at the saddle point, or even for a series of geometries along the reaction path.[67]

The value of Q_{vib} at temperature T is given by (where k is a Boltzmann constant)

$$Q_{vib} = exp\left(-E_0/kT\right)\left(\prod_{r=1}^{M}\left[1-exp\left(-\nu_r/kT\right)\right]\right)^{-1}, \tag{56}$$

where ν_r are the fundamental vibrational frequencies.

Evidently, Q_{vib} is a function of E_0, and its evaluation is a little tricky because it depends on both anharmonic constants and the Dunham constant term G_0, while each of these quantities are dependent on the choice of Fermi resonances. After summation of these two contributions (they both have partly phenomenological character due to the nature of Dunham expansion) we must obtain the correct value of E_0, which must be independent on any kind of vibrational resonances. Evidently, resonance terms present in G_0 and anharmonic constants mutually cancel each other, which obviates the need to remove such terms.[67] There is a number of publications with expressions for calculation of both G_0 and E_0.[5,20,42,68–71] The most recent publication by Rosnik and Polik[20] gives the an erroneous expression for G_0 (Eq. (77) in Ref. 20), as the last term but one should obviously be $-\frac{7}{576}\sum_k \phi_{kkk}^2\omega_k^{-1}$.

We have derived an alternative expression by comparing formulas for ZPVE from Refs. 68, 70, and 71. The former paper gives a more expanded expression while the latter works present a more compact form, which, however, is erroneous in the kinetic term. Taking the correct form of the kinetic term from Ref. 68, we obtain

$$\begin{aligned} E_0 = {} & \frac{1}{2}\sum_i \omega_i - \frac{1}{32}\sum_{ijk}\frac{\phi_{iik}\phi_{kjj}}{\omega_k} \\ & - \frac{1}{48}\sum_{ijk}\frac{\phi_{ijk}^2}{\omega_i+\omega_j+\omega_k} + \frac{1}{32}\sum_{ij}\phi_{iijj} \\ & - \frac{1}{4}\sum_{\alpha=x,y,z} B_e^{\alpha}\left[1-\sum_{i>j}\left(\zeta_{ij}^{\alpha}\right)^2\frac{(\omega_i-\omega_j)^2}{\omega_i\omega_j}\right]. \end{aligned} \tag{57}$$

Another attempt to rectify errors in the ZPVE expression[70,71] was made in Refs. 40 and 41, but the frequency ratio multiplier in their kinetic term is missing. Our comparison of numerical results obtained by this formula with ones calculated using numerical-analytic implementation of CVPT2 prove the correctness of the expression (57), which is therefore recommended for general use because it is resonance-free.

TABLE I. Vibrational Fermi resonances of formaldehyde in the first order of CVPT.[a]

No.	Resonance operator	Average Freq.	Denominator	S-coeff. Ξ_k	Ratio, $W_{12}/(E_2-E_1)$	Martin, exact	Martin, approx.	Effect of diagonalization
1	$1^{+1}3^{-2}$	3004.3	141.6	0.0985	0.1394	0.0514	0.0534	2.7491
2	$1^{+1}4^{-2}$	2657.1	552.8	0.1119	0.1583	0.3307	0.3471	13.8513
3	$1^{+1}6^{-2}$	2739.3	388.4	0.1124	0.1589	0.2360	0.2478	9.8113
4	$1^{+1}2^{-1}3^{-1}$	3126.3	385.5	0.0555	0.0555	0.0036	0.0036	1.1862
5	$2^{+1}5^{-1}6^{+1}$	3028.9	50.3	1.1159	1.1160	26.2810	78.0104	62.6369
6	$3^{+1}5^{-1}6^{+1}$	2906.9	193.7	0.3542	0.3542	2.4610	3.0471	24.2928

[a] All parameters, except dimensionless "*S*-coeff." and "Ratio," are given in units cm^{-1}.

III. NUMERICAL EXAMPLES AND DISCUSSION

In this section we consider practical numerical examples concerning two main issues discussed theoretically in Secs. II B and II C. First, we will determine if the commutator term $[S_1^*, H_1^\dagger]$ contributing to the correct expression for Darling-Dennison constants (Eq. (21)), is significant in specific cases and the degree of its importance. Two classic molecules will be used as examples for the study: formaldehyde ($H_2C{=}O$) and ethylene ($CH_2{=}CH_2$). Second, we will analyze the behavior of several Fermi resonance criteria in a model case of H_2O molecule and give practical recommendations.

A. The method of calculation

For formaldehyde and ethylene molecules, we employed essentially the same initial data and method of calculation as used in our preceding study devoted to vibrational polyads.[26] The CVPT2 calculations for both formaldehyde and ethylene molecules were accomplished with full quartic force fields obtained with the aid of MP2/aug-cc-pVTZ (formaldehyde) and MP2/cc-pVTZ (ethylene) QM models. The numerical-analytic operator CVPT computations were performed using our software package ANCO, described in detail in previous studies.[49–52] In order to improve the agreement between calculated and observed fundamentals and ensure a more accurate description of resonances, in the final stage of the CVPT2 calculation initial harmonic frequencies were replaced by values obtained from the advanced QM model CCSD(T)/cc-pVQZ. This approach corresponds to the concept of a "hybrid" force field,[72,73,52] wherein a quartic force field of a lower QM level is combined with the values of ω_r (harmonic frequencies) imported from higher-level QM calculations. The detection of Fermi and Darling-Dennison resonances was accomplished using the resonance index Ξ^* equal to 0.05.

B. Example No. 1: Fermi and Darling-Dennison resonances of formaldehyde

In case of this molecule, the chosen resonance criterion reveals 10 resonances in total, of which six are Fermi resonances (three of 1-2 Type and three of 1-11 Type), and four Darling-Dennison resonances (one of the 2-2 Type, two of 11-11 Type and one of 1-1 Type). Numerical-analytic evaluation of the commutator $[S_1^*, H_1^\dagger]$ indicates that these operators have no common terms. Tables I and II present the summary of results of calculation of all resonance coefficients. In these Tables, the column "*Effect*" denotes the "repulsion" of energy levels as a consequence of diagonalization of the 2×2 matrix,

$$\begin{gathered}
\begin{bmatrix} \bar{E}-\varepsilon & K \\ K & \bar{E}+\varepsilon \end{bmatrix}, \quad \bar{E} = \frac{E_2+E_1}{2}, \\
\varepsilon = \frac{E_2-E_1}{2}, \quad \lambda_{1,2} = \bar{E} \pm \Delta, \\
\Delta = \varepsilon\sqrt{1+\frac{K^2}{\varepsilon^2}}, \\
Effect = \Delta - \varepsilon = \frac{E_2-E_1}{2}\left(\sqrt{1+\frac{4K^2}{(E_2-E_1)^2}}-1\right).
\end{gathered} \tag{58}$$

We have found that in the case of formaldehyde the values of Darling-Dennison constants coincide within numerical accuracy for both VPT2 (analytical) and CVPT2 (numerical-analytic operator) versions. This result is consistent with the theoretical prediction made in Sec. II B that, if

TABLE II. Vibrational Darling-Dennison resonances of formaldehyde in the second order of CVPT.[a]

No.	Resonance operator	Average Freq.	Denominator	S-coeff. Ξ_k	Ratio $K_{12}/(E_2-E_1)$	K_{DD} perturbed	K_{DD} depert.	Effect of diagonalization
1	$1^{+2}5^{-2}$	5937.3	140.5	0.2560	0.5119	− 143.8439	− 143.8439	30.2877
2	$1^{+1}3^{+1}5^{-1}6^{-1}$	4373.7	194.7	0.1109	0.1109	− 6.3237	86.3493	2.3643
3	$1^{+1}6^{+1}3^{-1}5^{-1}$	4373.7	335.2	0.0652	0.0652	148.7082	87.4769	1.4206
4	$2^{-1}3^{+1}$	1659.5	244.0	0.0776	0.0287	6.9139[a]	− 6.9913[b]	0.2002

[a] All parameters, except dimensionless "*S*-coeff." and "Ratio," are given in units cm^{-1}.

[b] The value of matrix element itself is given.

TABLE III. Vibrational Fermi resonances of ethylene in the first order of CVPT.[a]

No.	Resonance operator	Average Freq.	Denominator	S-coeff. Ξ_k	Ratio, $W_{12}/(E_2 - E_1)$	Martin, exact	Martin, approx.	Effect of diagonalization
1	$1^{+1}2^{-2}$	3249.6	184.43	0.1467	0.2075	− 0.3152	− 0.3418	7.9399
2	$1^{+1}12^{-2}$	3053.5	207.67	0.1380	0.1951	− 0.2802	− 0.3012	7.9088
3	$2^{-1}10^{+2}$	1656.5	28.82	0.3163	0.4474	− 0.8421	− 1.1546	5.7690
4	$3^{+1}10^{-2}$	1504.6	274.98	0.0571	0.0808	− 0.0116	− 0.0117	1.7956
5	$1^{-1}2^{+1}3^{+1}$	3097.7	119.37	0.1246	0.1246	− 0.0279	− 0.0288	1.8545
6	$2^{+1}5^{-1}6^{+1}$	3068.6	309.33	0.2039	0.2039	− 0.4942	− 0.5345	12.8578
7	$2^{+1}11^{-1}12^{+1}$	3143.7	4.13	11.2706	11.2706	− 480.24	− 66661.4	524.7842
8	$6^{+1}9^{-1}12^{+1}$	2983.6	531.40	0.1458	0.1458	− 0.2305	− 0.2402	11.2987
9	$3^{+1}11^{-1}12^{+1}$	2991.8	299.67	0.1223	0.1223	− 0.0651	− 0.0670	4.4809
10	$7^{+1}8^{+1}12^{-1}$	1694.0	438.29	0.0834	0.0834	− 0.0209	− 0.0212	3.0460

[a] All parameters, except dimensionless "*S*-coeff." and "Ratio," are given in units cm^{-1}.

the commutator $[S_1^*, H_1^\dagger]$ is nil, VPT2 produces the correct result.

From Table I we can see that the resonance index Ξ_k varies within one order of magnitude (0.056–1.116, unitless), while Martin's criteria $\mathrm{X}^{(I)}$, $\mathrm{X}^{(II)}$ varies in the range of four orders of magnitude (0.004–26.28, in cm^{-1}). This wide range makes it difficult to choose a definitive value of Martin's criteria. There is another interesting result: for Fermi resonances, the ratio $\mathrm{P} = W_{12}/(E_2 - E_1)$ shows a very good correlation with the resonance index Ξ_k. Indeed, these quantities coincide for 1-11 resonances, for which the values of matrix elements are products of *W*-constants and a quantity $\sqrt{(v_r+1)(v_s+1)(v_t+1)}$, equal to unity for zero quantum numbers. However, 1-2 Fermi resonances are multiplied by a quantity $\sqrt{(v_r+1)(v_r+2)(v_s+1)}$ where the multiplier (v_r+2) originates from the second power in the resonance operator $\hat{F}_{rr,s} = W[(a_r^\dagger)^2 a_s + (a_r)^2 a_s^\dagger]$, and therefore the resonance index Ξ_k differs from the ratio $\mathrm{P} = W_{12}/(E_2 - E_1)$ by the factor $2^{1/2}$.

Inspection of Table II makes it possible to draw the following major conclusions. First, it is evident that except for the 2-2 resonance, all "perturbed" values of K_{DD} are substantially different from the correct ones. Another interesting conclusion concerns the correlation between Ξ_k coefficients and ratios $\mathrm{P} = H_{12}/(E_2 - E_1)$. For two 11-11 resonances, these ratios coincide with Ξ_k coefficients, because the multiplier inside the square root for corresponding matrix element $H_{rs,tu}(\bar{v}) = \frac{1}{4} K_{rs,tu} \sqrt{(v_r+1)(v_s+1)(v_t+1)(v_u+1)}$ is equal to unity for zero quantum numbers (see also general equation (47)). However, the ratio P for the 2-2 resonance is a double of the Ξ_k coefficient, since the same kind of multiplier in $H_{rr,ss}(\bar{v}) = \frac{1}{4} K_{rr,ss} \sqrt{(v_r+1)(v_r+2)(v_s+1)(v_s+2)}$ is equal to two. This interesting observation leads to a proposition that if the ratios $\mathrm{P} = H_{12}/(E_2 - E_1)$ are taken as the major resonance criterion, these quantities can be conveniently evaluated through Ξ_k coefficients by taking into account the powers of the CAO to which they correspond. The approach of this kind can be a subject of futures studies. This finding is especially interesting for bigger molecules, for which it is increasingly difficult to find a unique form of the polyad vector, that must be orthogonal to a subspace of resonance vectors, whose dimensionality must be exactly equal to $M - 1$.[26]

C. Example No. 2: Fermi and Darling-Dennison resonances of ethylene

For the molecule of ethylene, the chosen resonance criterion reveals ten Fermi resonances (four of 1-2 Type and six of 1-11 Type), and 26 Darling-Dennison resonances (six of the 2-2 Type, and 20 of the 11-11 Type). The summary of results is listed in Tables III and IV. Concerning Fermi resonances, the results obtained support the conclusions, drawn above for formaldehyde. There is one case when the resonance index Ξ_k is nearly equal for resonances $1^{-1}2^{+1}3^{+1}$ (0.1246) and $6^{+1}9^{-1}12^{+1}$ (0.1458), while Martin's criteria are different by an order of magnitude (0.0288 and 0.2402, respectively). A strong resonance $2^{+1}11^{-1}12^{+1}$ produces an abnormally high value (6.67×10^5 cm^{-1}) for the approximate version of Martin's criterion, while its exact form yields 480 cm^{-1}.

CVPT2 evaluation of the commutator $[S_1^*, H_1^\dagger]$ produces the following result:

$$[S_1^*, H_1^\dagger] = 5.7332\, a_3^\dagger a_9^\dagger a_5 a_{12} + 2.6501\, a_1^\dagger a_{12}^\dagger a_3 a_{11} - 1.3001\, a_6^\dagger a_{10}^\dagger a_7 a_8 + H.conj. \tag{59}$$

This means that the values of matrix elements obtained by the exact numerical-analytic version of CVPT2, corresponding to Darling-Dennison resonances $3^{+1}9^{+1}5^{-1}12^{-1}$, $1^{+1}12^{+1}3^{-1}11^{-1}$, and $6^{+1}10^{+1}7^{-1}8^{-1}$, must differ from the approximate treatment of VPT2, based on analytic formulas. Indeed (see Table IV), numerical values of K_{DD} are different; in one case ($3^{+1}9^{+1}5^{-1}12^{-1}$) an incorrect value is bigger by ~40%. Although this difference is not dramatic, we can draw an important conclusion that the previously overlooked effect of "interference" of Fermi and Darling-Dennison resonances must be taken into account.

As it is seen from the Table IV, in one case ($1^{+1}12^{+1}2^{-1}11^{-1}$) the "perturbed" value of K_{DD} is dramatically different (more than thirty times bigger) from the correct value, which means that careful accounting of Fermi resonances in the framework of traditional procedure of removing terms with resonance denominators is absolutely necessary.

There is also one small 1-1 Darling-Dennison resonance (not shown in the Table IV) between modes 2 and 3 with a matrix element connecting fundamental levels equal to -3.95 cm^{-1}. If resonance denominators are not removed, the

TABLE IV. Vibrational Darling-Dennison resonances of ethylene in the second order of CVPT.[a]

No.	Resonance operator	Average freq.	Denominator	S-coeff. Ξ_k	Ratio $K_{12}/(E_2-E_1)$	K_{DD}, perturbed	K_{DD}, depert.	K_{DD}, exact	Effect of diagonalization
1	$1^{+2}5^{-2}$	6380.7	131.75	0.1265	0.2529	– 66.6456	– 66.6456	– 66.6456	7.9485
2	$1^{-2}9^{+2}$	6406.7	183.81	0.0850	0.1700	– 62.5042	– 62.5042	– 62.5042	5.1683
3	$1^{+2}11^{-2}$	6299.1	31.50	0.4481	0.8963	– 56.4733	– 56.4733	– 56.4733	16.5811
4	$5^{+2}9^{-2}$	6472.6	52.06	0.3154	0.6307	– 65.6651	– 65.6651	– 65.6651	15.8698
5	$5^{+2}11^{-2}$	6364.9	163.26	0.0939	0.1878	– 61.3069	– 61.3069	– 61.3069	5.5658
6	$9^{+2}11^{-2}$	6391.0	215.31	0.0743	0.1486	– 64.0067	– 64.0067	– 64.0067	4.6562
7	$1^{-1}5^{-1}9^{+1}11^{+1}$	6385.8	10.28	5.6087	5.6087	– 230.5387	– 230.5387	– 230.5387	52.7253
8	$1^{+1}5^{-1}9^{+1}11^{-1}$	6385.8	41.78	1.4179	1.4179	– 236.9678	– 236.9678	– 236.9678	41.9271
9	$1^{+1}7^{-1}8^{+1}11^{-1}$	4106.1	1.90	1.2636	1.2636	– 9.5895	– 9.5895	– 9.5895	1.6296
10	$1^{+1}5^{-1}9^{-1}11^{+1}$	6385.8	173.53	0.3677	0.3677	– 255.2217	– 255.2217	– 255.2217	20.9348
11	$1^{+1}4^{+1}8^{-1}9^{-1}$	4201.4	8.63	0.2380	0.2380	8.2183	8.2183	8.2183	0.4641
12	**$1^{+1}3^{+1}11^{-1}12^{-1}$**	4570.5	92.00	0.1259	0.1259	**–12.0801**	**–46.3233**	– 46.3233	1.4354
13	$1^{-1}4^{-1}5^{+1}7^{+1}$	4197.2	17.01	0.1123	0.1123	7.6413	7.6413	7.6413	0.2119
14	$1^{+1}7^{+1}8^{-1}11^{-1}$	4106.1	33.40	0.0845	0.0845	– 11.2908	– 11.2908	– 11.2908	0.2369
15	$1^{-1}3^{-1}5^{+1}6^{+1}$	4495.4	58.20	0.0722	0.0722	16.8105	16.8105	16.8105	0.3019
16	**$1^{+1}12^{+1}3^{-1}11^{-1}$**	4570.5	123.51	0.0711	0.0818	**–356.7138**	**–40.4188**	**–35.1187**	**0.8213**
17	**$1^{+1}12^{+1}2^{-1}11^{-1}$**	4722.4	180.30	0.0580	0.0580	**–1276.2398**	**–41.8157**	– 41.8157	0.6041
18	**$2^{+1}5^{-1}9^{+1}12^{-1}$**	4809.2	222.08	0.0574	0.0574	**–0.9703**	**–50.9580**	– 50.9580	0.7284
19	$3^{+1}5^{+1}9^{-1}12^{-1}$	4657.3	133.78	0.0600	0.0600	– 32.1343	– 32.1343	– 32.1343	0.4807
20	**$3^{+1}9^{+1}5^{-1}12^{-1}$**	4657.3	81.73	0.0984	0.1335	**–30.4153**	**–43.6451**	**–32.1787**	**1.4317**
21	$3^{+1}6^{-1}9^{-1}11^{+1}$	4500.5	16.42	0.2285	0.2285	15.0095	15.0095	15.0095	0.8169
22	$4^{+1}7^{-1}9^{-1}11^{+1}$	4202.3	24.77	0.0989	0.0989	9.7959	9.7959	9.7959	0.2398
23	$4^{+1}5^{-1}8^{-1}11^{+1}$	4180.5	18.91	0.0884	0.0884	6.6860	6.6859	6.6859	0.1466
24	$5^{+1}7^{+1}8^{-1}9^{-1}$	4192.9	8.38	0.7846	0.7846	– 26.2950	– 26.2949	– 26.2949	3.6058
25	$5^{+1}7^{-1}8^{+1}9^{-1}$	4192.9	43.68	0.1364	0.1364	– 23.8268	– 23.8268	– 23.8268	0.7978
26	**$6^{+1}10^{+1}7^{-1}8^{-1}$**	1988.6	150.93	0.0752	0.0709	**–46.3202**	**–42.8246**	**–45.4248**	**0.7556**

[a] All parameters, except dimensionless "*S*-coeff." and "Ratio," are given in units cm^{-1}.

value becomes 100.7 cm^{-1}, which would cause a significant shift of fundamental levels (over 30 cm^{-1}).

D. Model case: 1-2 Fermi resonance in water: Comparison of resonance parameters

Our final numerical study is the comparison of the behavior of different resonance parameters (such as resonance index Ξ_k, Martin's criteria $X^{(I)}$, $X^{(II)}$, the ratio of the coupling coefficient to the difference in energy levels $P = H_{12}/(E_2 - E_1)$) and their correlation to the error in predicted frequencies, introduced by inclusion or exclusion of a certain resonance into explicit special consideration. We studied a numerical example, realistically modeling the classical 1-2 (ν_1–$2\times\nu_2$) Fermi resonance for the H_2O molecule. We employed a modified quartic force field calculated by the quantum-mechanical model MP2/aug-cc-pVTZ. Before proceeding to the analysis of Fermi resonance, it is worthwhile mentioning that our calculation predicts the value -147.67 cm^{-1} for the Darling-Dennison constant K_{DD}, which closely (error $<1\%$) agrees with the classical experimental value of $|K_{DD}| = 148.92$ cm^{-1}.[48]

For isolation of this resonance from unwanted couplings with a 2-2 resonance ($2\nu_1$–$2\nu_3$), all cubic and quartic force constants for the third normal coordinate q_3 (B_2) were set equal to zero. The values of surviving parameters of the Hamiltonian are as follows:

(1) Quadratic force constants (cm^{-1}):
$\omega_1 = 3821.88$, $\omega_2 = 1628.37$, $\omega_3 = 3947.71$.
(2) Cubic force constants (cm^{-1}):
$\varphi_{111} = -1790.40$, $\varphi_{112} = 77.97$, $\varphi_{122} = 313.03$, $\varphi_{222} = -250.69$.
(3) Quartic force constants (cm^{-1}):
$\varphi_{1111} = 752.47$, $\varphi_{1112} = -63.68$, $\varphi_{1122} = -305.40$, $\varphi_{1222} = 154.61$, $\varphi_{2222} = -44.35$.
(4) Vibration-rotation parameters (B_e^α in cm^{-1}, ζ_{rs}^α dimensionless):
$B_e^x = 9.4488$, $B_e^y = 26.9476$, $B_e^z = 14.5509$, $\zeta_{13}^x = 0.0116$, $\zeta_{23}^x = 0.9999$.

For the ν_1–$2\nu_2$ Fermi resonance the harmonic frequency denominator $\Delta = |\omega_1 - 2\omega_2|$ is equal to 565 cm^{-1}, and the value of the resonance index is equal to 0.0979. We varied ω_2 from its original value up so that the denominator was gradually decreased to a minimum value of 25 cm^{-1} in steps of 5 cm^{-1}. At each point, the error $\varepsilon = \nu_1^\dagger - \nu_1$ introduced by the perturbation treatment of this resonance was measured as a difference between two types of solutions as indicated below. Since there is a small local minimum of $\varepsilon = 0.1785$ near the value of the denominator $\Delta = 400$ cm^{-1}, we excluded results above this value for the reason that we also analyzed the inverted dependence of resonance parameters as functions of the error.

Solution A. The presence of the Fermi resonance was ignored, and all terms are treated as perturbations. This corresponds to inclusion of the middle term in the square brackets in the expression for the anharmonic constant

$$x_{rr} = \frac{1}{16}\phi_{rrrr} - \frac{1}{32}\sum_{s=1}^{M}\phi_{rrs}^2\left[\frac{1}{2\omega_r+\omega_s} - \frac{1}{2\omega_r-\omega_s} + \frac{4}{\omega_s}\right]. \tag{60}$$

After calculation of all anharmonic constants the values of $\nu_1^\dagger$ and $2\nu_2^\dagger$ were calculated using the standard Dunham-type expansion of Eq. (17). The diagonalization of the Hamiltonian matrix was not performed as it was already fully diagonal.

Solution B. The Fermi resonance was accounted for by the usual two-step procedure (VPT2+*W*). Anharmonic constants were calculated with exclusion of the middle resonant terms in the expression of Eq. (60) above, yielding "deperturbed" values,

$$x_{rr}^* = \frac{1}{16}\phi_{rrrr} - \frac{1}{32}\sum_{s=1}^{M}\phi_{rrs}^2\left[\frac{1}{2\omega_r+\omega_s} + \frac{4}{\omega_s}\right]. \tag{61}$$

Afterwards, deperturbed values of ν_1^* and $(2\times\nu_2)^*$ were calculated, as usual. Accounting for the Fermi resonance was properly accomplished through the variational diagonalization of the 2 × 2 Hamiltonian matrix with a Fermi resonance constant of $W = \frac{1}{4}\phi_{122}$, yielding the final values of ν_1 and $2\nu_2$. At each point of the calculation, defined by the value of the resonance denominator (in cm^{-1}), the following parameters were calculated:

(1) The value of error, introduced by the perturbative accounting for the resonance instead of its correct variational (†) treatment: $\varepsilon = \nu_1^\dagger - \nu_1$.

(2) The value of the dimensionless resonance index Ξ, multiplied by 20 to provide commensurate comparison with other parameters, expressed in cm^{-1},

$$\Xi_{122}^{(20\times)} = (20\times)\frac{\sqrt{2}}{8}\left|\frac{\phi_{122}}{\omega_1 - 2\omega_{22}}\right|. \tag{62}$$

(3) The values of Martin's resonance criterion $X^{(I)}$ in two forms, exact ($X_2^{(I)}$) and approximate ($X_4^{(I)}$), where subscript corresponds to the power of ϕ_{122} (see Sec. (II C) above).

(4) The value of an additional resonance criterion *Z*, introduced in one of our previous papers.[74] This criterion determines the effect of the perturbation contribution of cubic force constants φ_{kkl}, φ_{klm}, corresponding to a certain Fermi resonance, to the final value of the related fundamental frequency ν_k. The effects $Z_k^{(I)}$ and $Z_k^{(II)}$, when accounting for the Types I and II Fermi resonances on ν_k by the removal of the corresponding "offending" terms in the anharmonic constants and using the "deperturbed" constants x_{ii}^*, x_{ij}^*, are given by[72]

$$Z_k^{(I)} = \nu_k^* - \nu_k = \frac{\phi_{iik}^2}{16\Delta_{iik}}, \quad Z_k^{(II)} = \nu_k^* - \nu_k = \frac{\phi_{ijk}^2}{8\Delta_{ijk}}. \tag{63}$$

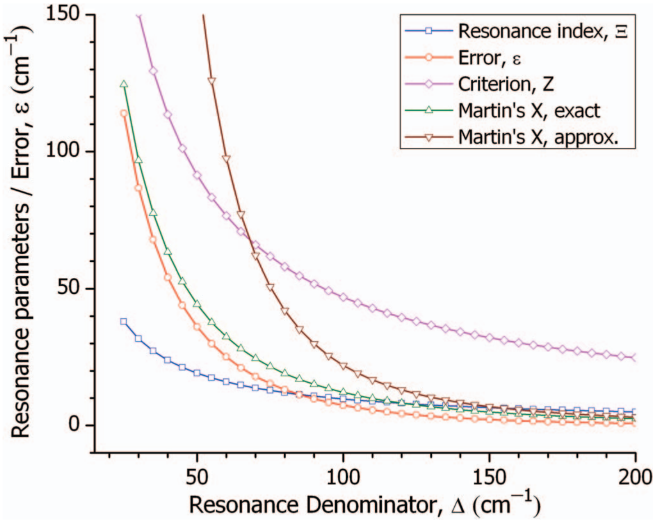

FIG. 1. Functional dependence of five resonance parameters on the strength of the Fermi resonance (ν_1–$2\nu_2$) for the H_2O molecule. The strength is changed by variation of ω_2 in the resonance denominator $\Delta = |2\omega_2 - \omega_1|$.

All five parameters described above are displayed on Fig. 1 graphically. Visual inspection of this figure instantly shows that there is a very good correlation between the resonance index and the exact form of Martin's criterion $X^{(I)}$. However, an approximate form of Martin's criterion is correlated more poorly. The additional resonance criterion $Z_k^{(I)}$ shows generally good correlation with the resonance index, but has a systematic shift.

In order to clarify the fine details of behavior of different resonance criteria, the functional dependences were inverted in such a way that the error (ε) became the abscissa of the graph and the other parameters became ordinates. Evidently, such a graph should show the dependence of all resonance parameters as a function of the acceptable error, introduced by an improper treatment of a certain resonance. The new form of these functional dependencies is displayed in Fig. 2 with an enlarged scale for a general overview and in Fig. 3 on a smaller scale. It is evident that both Martin's criteria have

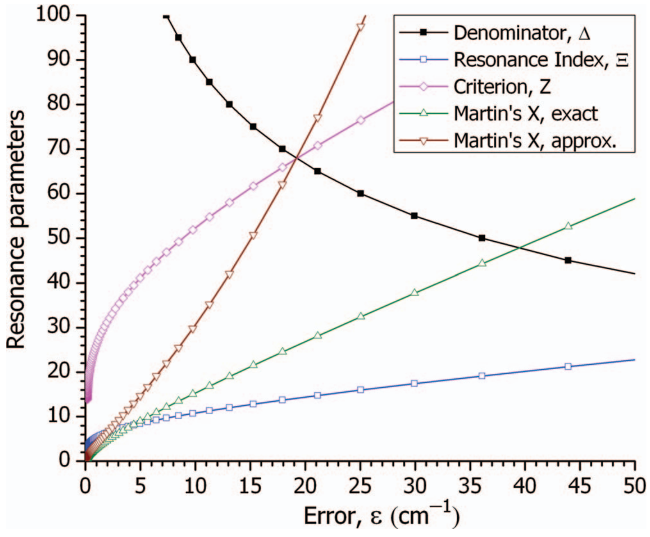

FIG. 2. Functional dependence (general overview) of five resonance parameters on the error, introduced by an improper treatment of Fermi resonance (ν_1–$2\nu_2$) for the H_2O molecule.

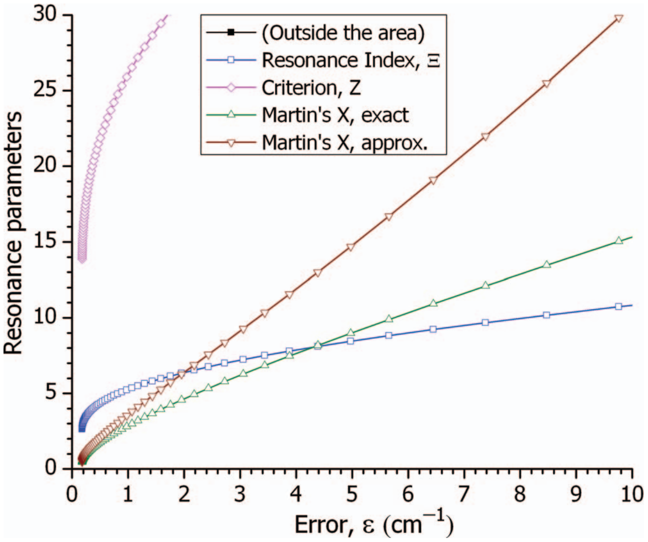

FIG. 3. Functional dependence (enlarged view) of five resonance parameters on the admitted error, introduced by an improper treatment of Fermi resonance (ν_1–$2\nu_2$) for the H_2O molecule.

more-or-less linear behavior as a function of acceptable error, while the resonance index behaves rather as a square root function. If an acceptable error is 1 cm^{-1}, then the value of corresponding Martin's criteria is about 3 cm^{-1}. We can conclude that the value of $X^{(I)} = 1\ \mathrm{cm}^{-1}$, suggested earlier in Ref. 38, would have provided a good accuracy of 0.25 cm^{-1} in this case. The resonance index changes sharply for smaller values of the acceptable error and for very big values of error stays almost unaltered. In this particular case the acceptable error of 1 cm^{-1} corresponds to the value of resonance index equal to 0.26, and the error of 0.5 cm^{-1} corresponds to 0.22.

IV. CONCLUSIONS

The literature provides analytical expressions, within the second-order perturbation theory, for Darling-Dennison resonance coupling coefficients (K_{DD}) of different types (2-2, 2-11, 11-11, 1-3, 1-21, 1-111, 1-1).[16–20] These expressions include denominators with linear combinations of harmonic frequencies, originating from the first-order Fermi resonances. Ignoring abnormally small values of these denominators can lead to anomalous values of K_{DD}, and a manual removal of such terms had been suggested as the remedy.[17,20,46,47]

For the first time, we have proven theoretically and demonstrated numerically that, in certain cases this treatment may produce incorrect results. Precisely speaking, a commutator term $[S_1^*, H_1^\dagger]$ (see Eq. (21) and explanation in Sec. II B) is responsible for the difference between previously used analytic expressions and a correct result, which properly accounts for the presence of Fermi resonance effects in K_{DD}. It is difficult to ensure full accounting of this effect in the form of analytic formulas. The reason is that breaking down the cubic terms of the original Hamiltonian into resonant $H_1^\dagger$ and non-resonant terms, eliminated with the aid of operator S_1^*, cannot be done before numerical values of Hamiltonian constants are known. A numerical-analytic implementation of CVPT is capable of handling this situation and producing correct K_{DD} values. A numerical example with the ethylene molecule has convincingly proven the correctness of the theoretical predictions.

Generally speaking, the set of formulas and procedures needed for a numerical-analytic implementation of CVPT is rather compact in comparison to the traditional sets of formulas, thereby making the CVPT option preferable, at least for molecules of medium size (up to 10-12 atoms), for which the volume of intermediate data is small enough (a few gigabytes of a hard disk space) and the speed of calculations on a desktop computer is sufficiently fast (a few hours). For molecules of much bigger size (tens of atoms), VPT2 in a traditional implementation is a preferred option for economical reasons. We have implemented both methods in the framework of the same software package (ANCO) to simplify verification of results and to facilitate easy switching between these methods.

Another part of the problem associated with both Fermi and Darling-Dennison resonances is having a reliable method for deciding if a particular coupling is a resonance. We analyzed a widely used Fermi resonance criterion introduced by Martin *et al.*[45] and advocated by Barone's group.[5,38,40] This criterion is usually expressed in a truncated form as the leading term of the Taylor expansion (Eqs. (39) and (40) above). Our study shows that it is much better to employ this criterion in its full form. The model case (H_2O) shows that the functional dependency of both forms of Martin's criteria from the acceptable error as an argument has a nearly linear character in a wide range of variation of the error (see Fig. 3). For example, the truncated form of Martin's criterion can be multiplied by a factor of approximately 3.0 and then this functional dependency gains the simple linear form $f(x) \approx x$, and for the full form of Martin's criterion this coefficient is equal to ≈2.0.

For the Darling-Dennison resonances in formaldehyde and ethylene, the detailed comparison of the values of the resonance index, constants K_{DD} themselves and coupling coefficient to energy difference ratio $\mathrm{P} = H_{12}/(E_2 - E_1)$ leads to the conclusion that the most universal resonance criterion is the latter ratio. This ratio can be accurately calculated by numerical-analytic implementation of CVPT2 and also with sufficient accuracy for practical needs by a set of analytic formulas of VPT2. A typical value of this ratio, indicating the presence of a resonance at any order or type, is 1/10, which means that the resonance-free case takes place when the difference in energy levels is an order of magnitude larger than the corresponding matrix coupling coefficient. This universal criterion of resonances obviates the need to specify case-specific resonances parameters.[38] A definitive answer (yes or no) about any particular coupling can be made with the aid of additional polyad analysis.[21,26] Finally, it should be noted that the model considered is based on the concept of normal modes with rectilinear finite displacements of atoms from the equilibrium point and the corresponding Watson Hamiltonian. Alternative perturbative approaches can employ other types of coordinate representations and Hamiltonians, in the framework of which the resonance effects will also occur, but the form of resonance operators and corresponding numerical coefficients will be different.

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