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# DOORWAY models in the inverse problem for a complex vibronic analogue of the Fermi resonance

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We solve the inverse problem for the complex Fermi resonance or its vibronic analogue, and to this end we use the matrix $XEX^t$, where $E = \mathrm{diag}(\{E_k\})$ is a diagonal matrix, $E_k$ are the energies of the observed „conglomerate“ of lines, and the intensities of these lines $I_k$ determine the first row of the matrix $X$, $(X_{1k})^2 = I_k$ $k = 1, 2, \dots, n$, $n \geq 3$. Hamiltonian matrix of the direct model, $H^{\mathrm{DIR}}$, whose parameters are the energies of pre-diagonalized „dark“ states, $A_i$, and the matrix elements of their coupling to the „bright“ state, $B_i$, $(i = 1, 2, \dots, n-1)$, is obtained after the diagonalization of the $XEX^t$ block, which belongs to the „dark“ states. We show that Hamiltonian matrix with the single doorway state (DW), $H^{\mathrm{DW1}}$, can be obtained from the matrices $H^{\mathrm{DIR}}$ or $XEX^t$ by first step of the Householder triangularization, i.e. by similarity transformation with a reflection matrix constructed by quantities $B_i$ or $D_i = (XEX^t)_{1,i+1}$. For the energy of the first DW1 state, $g_1$, and the matrix element of its coupling to the „bright“ state, $w_1$, the use of the Householder transformation gives: $g_1 = \Sigma_{i=1}^{n-1} B_i^2 A_i / (\Sigma_{j=1}^{n-1} B_j^2) = \Sigma_{k=1}^{n} E_k^3 I_k / \Sigma_{l=1}^{n} E_l^2 I_l$, $|w_1| = (\Sigma_{i=1}^{n-1} B_i^2)^{1/2} = (\Sigma_{k=1}^{n} E_k^2 I_k)^{1/2}$. In similar way, using the Householder transformation, the Hamiltonians for the models with several doorway states, $H^{\mathrm{DW2}}, H^{\mathrm{DW3}}, \dots, H^{\mathrm{DW}(n-1)}$, are successively obtained. The Hamiltonian of the DW$(n-2)$ model is represented by a symmetric tridiagonal matrix $H^{\mathrm{DW}(n-1)}$, its diagonal elements $g_i$ determine the energies of the DW1-, DW2-, …, DW$(n-1)$ states, and the off-diagonal elements $w_i$ determine the corresponding coupling between them.

**Keywords:** vibronic coupling, complex vibronic analogue of the Fermi resonance, inverse problem, Householder transformation, doorway models.

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## Introduction

Complex vibronic analogue of the Fermi resonance (a term introduced by Herzberg [1]) is characterized by proximity of energies of $\varphi_1$ electronic-vibrational state ($\varphi_1 = \varphi'_{\mathrm{el}}\varphi'_{\mathrm{vib},1}$, $\varphi'_{\mathrm{el}}$ — the „upper“ electronic state) and a number of $\varphi_m$ electronic-vibrational (vibronic) states ($\varphi_m = \varphi''_{\mathrm{el}}\varphi''_{\mathrm{vib},m}$, $\varphi''_{\mathrm{el}}$ — the „lower“ electronic state). The effect of nonadiabatic electronic-vibrational interaction results in splitting of quasi-degenerate levels and redistribution of the intensity of transition from the ground state, $\varphi_0 \to \varphi_1$, to transitions to perturbed states, $\varphi_0 \to \Psi_k$ (Fig. 1). For the Fermi resonance itself [1–4] there are only two actual states: these are vibrational states of the same electronic state, and their interaction is a result of the anharmonic coupling of vibrations. Similar energy level proximity of quasi-degenerate states, which are different in their physical nature, is significant for such phenomena as autoionization, predissociation, non-radiative transitions in polyatomic molecules, photoionization dynamics, intramolecular vibrational energy redistribution [1–3,5–7].

A typical example of manifestation of the complex vibronic analogue of the Fermi resonance are the absorption (fluorescence excitation) spectra that correspond to the $0{-}0$-transition of $S_0 \to S_2$ to the second singlet state of molecule, when instead of the expected one line a complicated „conglomerate“ is observed consisting of narrow lines with large number of components and irregularly distributed frequencies and intensities. This takes place in low-temperature absorption spectra of naphthalene molecule embeded as an impurity center into durene or xylene crystals, where number of components is not less than 50 [8]. In a similar way in fluorescence excitation spectra of some porphyrinic compounds, in matrices of saturated hydrocarbons at 4.2 K the $0{-}0$-transition of $S_0 \to S_2$ is distributed over $\sim 30$ components [9,10]. The coupling between states can be more complicated as well, for example, as a result of vibronic and spin-orbital interaction between the first excited singlet state $S_1$ and energy-close vibrationally excited triplet states. This causes the observed complex structure in high-resolution rotational fluorescence-excitation spectra of pyrazine [11,12], methyl derivatives of pyrimidine [13], acetylene [14]. The complex vibronic analogue of the Fermi resonance manifests for a number of other molecular systems (some references are given in [15]).

Calculations of the complex spectra resulted from the vibronic coupling were made with the involvement of quantum chemistry methods in [16–18]. However, in solving this problem, the condition of resonance requires electronic and vibrational states to be calculated with a high accuracy. In this context an inverse problem (spectral deconvolution) can be formulated, where matrix elements of the Hamiltonian of vibronic interaction in the resonance conditions must be determined from experimental data. It is essential that the inverse problem assumes that in the zero-order approximation only one transition is allowed from among all the considered transitions, i.e. the transition to the „bright" state, while other transitions, i.e. transitions to „dark" states, are forbidden (Fig. 1).

The spectral deconvolution problem seems quite unusual, and to solve it initially the trial-and-error method was applied (for naphthalene [8,19], pyrazine [20]). In [21–24] the inverse problem in question was solved using the formalism of the Green's function, and later, for the case of discrete „dark" states, the method of direct-coupling model was formulated [25–27]. Within this model a set of energies of (prediagonalized) „dark" states and squared matrix elements of their coupling with the „bright" state is determined. In [24,28], in relation to non-radiative transitions and the intramolecular vibrational energy redistribution (IVR) the spectral deconvolution was expanded to another class of model Hamiltonians with accentuated importance of characteristics of the dynamic process that takes place after the excitation through a distinct, intermediate (doorway, DW) „dark" state. These doorway-coupling model Hamiltonian take into account the interaction among „dark" states. In [29,30] the direct-coupling model was applied to massive spectral datasets for molecules of trifluoropropyne, acetylene, as well as to model spectra, and the authors have came to the conclusion that this model needs to be modified by explicit consideration of the interaction in the block of „dark" states. In [31] it is shown that the transition from the direct-coupling Hamiltonian to the doorway-coupling Hamiltonian can be achieved within the formalism of the Green's function, parameters of the first DW1-state were calculated through spectral moments.

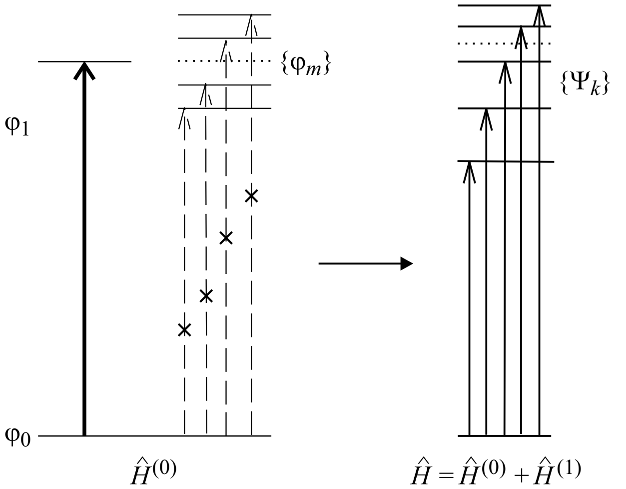

**Figure 1.** Diagram of the complex vibronic analogue of the Fermi resonance. The action of $\hat{H}^{(1)}$ perturbation results in redistribution of intensity from the transition to the „bright" state $\varphi_0 \to \varphi_1$ towards the transitions to perturbed states $\varphi_0 \to \Psi_k$. $\{\varphi_m\}$ are „dark" states.

In our studies [15,32] the inverse problem in the direct-coupling model is solved on the basis of methods typical for the algebraic eigenvalue problem [33], where first of all the intensity redistribution at a resonance of Fermi type was taken into account. They are used to recover the Hamiltonian matrix, which actual elements define the energies of pre-diagonalized „dark" states and their direct coupling with the „bright" state. In this study we have presented an algorithm to solve the inverse problem for the complex Fermi resonance or its vibronic analogue for the model with one or more intermediate doorway-states. For these purposes we used the Householder transformation that is applied in the algebraic matrix eigenvalue problem when it is tridiagonalized [33].

## General problem formulation

We shall consider resonance interactions of excited states of a molecule due to perturbation $\hat{H}^{(1)}$ within the linear variation method where wave functions $\Psi_k$ are taken in the following form:

$$\Psi_k = \Sigma_{l=1}^{n} C_{lk}\varphi_l = C_{1k}\varphi_1 + \Sigma_{m=2}^{n} C_{mk}\varphi_m,$$

where $\varphi_1$ is the „bright" state, $\varphi_m$ $(m = 2, 3, \ldots, n)$ are „dark" states. Functions $\varphi_l$ are eigenfunctions of the zero-order approximation Hamiltonian, $\hat{H}^{(0)}\varphi_l = \varepsilon_l\varphi_l$; for these functions an exact or approximate degeneracy takes place. The well-known direct problem consists in calculating $H$ matrix elements, $\langle\varphi_l|\hat{H}|\varphi_k\rangle = \langle\varphi_l|\hat{H}^{(0)} + \hat{H}^{(1)}|\varphi_k\rangle$, and solving the secular problem:

$$HC = CE, \quad E = \mathrm{diag}(E_1, E_2, \ldots, E_n). \tag{1}$$

We shall assume basis functions $\varphi_l$ as real functions, then $H$ is a symmetric matrix and $C$ matrix of coefficients $C_{lk}$ is an orthogonal matrix, $C^{-1} = C^t$ (here and elsewhere $t$ superscript denotes transposition).

The intensity of transitions from the ground state $\varphi_0$ to the perturbed excited states $\Psi_k$ is proportional to $|\langle\Psi_k|\mathbf{M}|\varphi_0\rangle|^2$, where $\mathbf{M}$ is operator of the dipole moment of the molecule. The action of perturbation results only in redistribution of $\varphi_0 \to \Psi_k$ transitions intensity as compared to $\varphi_0 \to \varphi_l$, while $\Sigma_{k=1}^{n}|\langle\Psi_k|\mathbf{M}|\varphi_0\rangle|^2 = \Sigma_{l=1}^{n}|\langle\varphi_l|\mathbf{M}|\varphi_0\rangle|^2$. In the case when in the zero-order approximation only one transition is allowed among all the transitions from the ground state to the excited state, i.e. the $\varphi_0 \to \varphi_1$ transition, and other $\varphi_0 \to \varphi_m$ transitions are forbidden (Fig. 1), the relative intensity of $\varphi_0 \to \Psi_k$ transition is:

$$I_k = |\langle\Psi_k|\mathbf{M}|\varphi_0\rangle|^2/|\langle\varphi_1|\mathbf{M}|\varphi_0\rangle|^2 = (C_{1k})^2.$$

In the inverse problem matrix elements of the Hamiltonian $\langle\varphi_l|\hat{H}|\varphi_k\rangle$ must be determined from the observed data: energies $E'_k$ and intensities $I'_k$ of transitions. The total number of $E'_k$ and $I'_k$ items is $2n$, but due to the condition of $\Sigma_{k=1}^{n} I_k = 1$, where $I_k = I'_k/\Sigma_{l=1}^{n} I'_l$ is the relative intensity, their number becomes $2n - 1$. The number of elements in the $H$ matrix is $n(n+1)/2$, and it means that restrictions has to be imposed on its form at $n \geq 3$. There are no restrictions for the simple Fermi resonance or its vibronic analogue with $n = 2$. If the „bright" state is the only one state, the calculated relative intensity $(C_{1k})^2$ should be equal to the relative experimental intensity $(C_{1k})^2 = I_k$, while the $\Sigma_{k=1}^{n} I_k = 1$ normalizing corresponds to the $\Sigma_{k=1}^{n}(C_{1k})^2 = 1$ normalizing. Now we shall determine the „center of gravity" of observed energies, $G = \Sigma_{k=1}^{n} E'_k I_k$, and then all energies will be calculated from this center, $E_k = E'_k - G$, then $\Sigma_{k=1}^{n} E_k I_k = 0$. The last equation for calculated values corresponds to the equation of $\Sigma_{k=1}^{n} E_k (C_{1k})^2 = H_{11} = 0$, which is a consequence of orthogonality of the $C$ matrix. Thus, the „center of gravity" $G$ of the observed conglomerate should coincide with the energy of the „bright" state in relation to the ground state.

The intensity of $\varphi_0 \rightarrow \Psi_k$ transitions is defined by elements of the first row of $C$ matrix only, which means that the selection of basis functions of „dark" states $\varphi_m$ is ambiguous. This circumstance is used to avoid the difficulties related to the fact that the number of experimental values is insufficient to determine matrix elements $\langle \varphi_l | \hat{H} \varphi_k \rangle$ at $n \geq 3$. Specifically, if we change over from functions $\varphi_m$ to functions $\Phi_m$ that diagonalized the „dark" states block of matrix $H$, the matrix can be represented in a form known as canonical [19,21]:

$$H = \begin{pmatrix} 0 & B^t \\ B & A \end{pmatrix}, \qquad (2)$$

where $A = \mathrm{diag}(A_1, A_2, \ldots, A_{n-1})$ is a $(n-1) \times (n-1)$ diagonal matrix, $A_i = \langle \Phi_{i+1} | \hat{H} | \Phi_{i+1} \rangle$, $B$ is a column vector of size $n-1$, $B^t = (B_1, B_2, \ldots, B_{n-1})$, $B_i = \langle \Phi_{i+1} | \hat{H} | \varphi_1 \rangle = \langle \Phi_{i+1} | \hat{H}^{(1)} | \varphi_1 \rangle$, $i = 1, 2, \ldots, n-1$. The number of values $\{A_i\}$ and $\{B_i\}$ and the number of experimental values $\{E_k\}$ and $\{I_k\}$ taking into account two conditions of $\Sigma_{k=1}^{n} E_k I_k = 0$ and $\Sigma_{k=1}^{n} I_k = 1$ is equal to $2n-2$, therefore the problem of Hamiltonian matrix recovery in form (2) must have an unambiguous solution. Representation of matrix $H$ in form (2) defines the direct-coupling model $H \equiv H^{\mathrm{DIR}}$.

In our studies [15,32] we have developed a method to solve the spectral deconvolution problem, where at the first step an orthogonal matrix $X$ with its first row meeting the condition of $(X_{1k})^2 = I_k$ for intensities and the $XEX^t$ matrix, $E = \mathrm{diag}(\{E_k\})$ are constructed; at the second step, with taking into account the requirement of absence of „interaction" between „dark" states, the direct-coupling model matrix $H$ (2) is derived from matrix $XEX^t$ by similarity transformation. The goal of this study is to apply the Householder method of real symmetric matrix triangularization [33] to build up Hamiltonian matrices of models with one or more doorway-states. We shall show that the main step in getting on to the Hamiltonian matrix with one doorway-state $H^{\mathrm{DW1}}$ from the matrix $H$ (or from $XEX^t$) is implemented by similarity transformation of reflection matrix composed of $B_i$ values (or $D_i = (XEX^t)_{1,i+1}$), $i = 1, \ldots, n-1$. Then Hamiltonian matrices of models with several doorway-states will be successively derived using analogous similarity transformation.

## Taking into account the redistribution of intensity. Direct-coupling model Hamiltonian matrix

In [32] it is noted that for the special case of matrix $H$ in form (2), that is at $A_i = a = \mathrm{const}$, the first row of eigenvectors has only two non-zero values. This corresponds to a redistribution of intensity from the initial transition to the „bright" state $\varphi_0 \rightarrow \varphi_1$ only to two transitions, but then each of them can be considered as a source of redistribution to another two transitions, and so on (Fig. 2). In [32] it is shown how for each step of intensity „splitting" the parameters $a$, $\{B_i\}$ should be calculated from combinations of observed values $\{E_k\}$ and $\{I_k\}$; the procedure includes diagonalization of intermediate matrices as well. Finally, an orthogonal matrix $X$ is obtained where square of the first row elements is equal to the intensity of observed lines, $(X_{1k})^2 = I_k$. Another streamlined algorithm to build up the $X$ matrix with the same condition $(X_{1k})^2 = I_k$ is proposed in [15], where this matrix is represented as a product of elementary plane Jacobi rotation matrices, which also corresponds to the successive redistribution of intensities starting from „splitting" for the initial transition $\varphi_0 \rightarrow \varphi_1$ (Fig. 2).

It is evident that orthogonal matrices $X$ obtained by the algorithms illustrated in Fig. 2, $a$ and $b$ are different from each other, identical is only the relationship of $(X_{1k})^2 = I_k$. Also, a sufficiently large set of orthogonal matrices $X$ can be obtained on the basis of combination of type $2a$ and $2b$ algorithms (however, there is no practical necessity in it), which is related to the multiplicity of choice of linear combinations of „dark" state functions not affecting the intensity of $\varphi_0 \rightarrow \Psi_k$ transitions.

Once the $X$ matrix is defined, let us perform the $XEX^t$ similarity transformation of the diagonal matrix $E$ composed of observed energies $E_k$, $E = \mathrm{diag}(E_1, E_2, \ldots, E_n)$, which results in that the $XEX^t$ takes the following block form:

$$XEX^t = \begin{pmatrix} 0 & D^t \\ D & F \end{pmatrix}, \qquad (3)$$

where $F$ is a $(n-1) \times (n-1)$ symmetric real matrix, $D$ is a column-vector of size $n-1$. Then, an eigenproblem can be formulated for the $F$ matrix:

$$FZ = ZA, \quad A = \mathrm{diag}(A_1, A_2, \ldots, A_{n-1}). \qquad (4)$$

Taking into account that $F = ZAZ^t$, $Z^t = Z^{-1}$, by multiplying (3) from the left by $Y$ and from the right by $Y^t$, where

$$Y = \begin{pmatrix} 1 & 0 \\ 0 & Z^t \end{pmatrix},$$

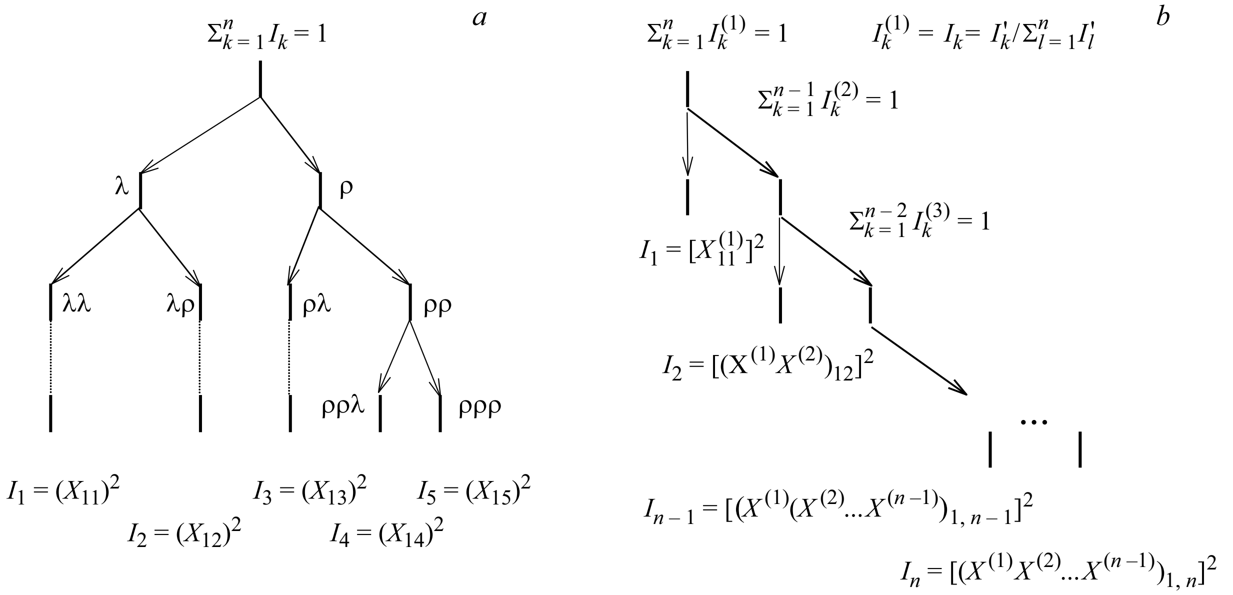

**Figure 2.** Redistribution of transition intensities according to the algorithm of [32] (for $n = 5$) and the algorithm of [15] ($X^{(i)}$ is elementary Jacobi rotations).

we get the $H$ matrix with required structure (2):

$$H = (YX)E(YX)^t,$$

i.e. $H$ is diagonalized by the $C = YX$ matrix. In this case the first row of matrix $C$ coincides with the first row of matrix $X$, $C_{1k} = X_{1k}$, and, hence, the requirement for intensities is fulfilled, $(C_{1k})^2 = (X_{1k})^2 = I_k$. Vector $B$ is calculated from vector $D$, $B = Z^t D$. Thus, energies of „dark" states are represented by eigenvalues of $A_i$ of problem (4), while matrix elements of coupling $B_i$ of „bright" $\varphi_1$ and „dark" $\Phi_{i+1}$ states are calculated by the following formula: $B_i = \Sigma_{j=1}^{n-1} D_j Z_{ji}$.

With neglecting the coupling between „dark" states due to the $\hat{H}^{(1)}$ perturbation, i. e. with equating basis $\Phi_{i+1}$ and basis $\varphi_{i+1}$, diagonal elements $A_i$ can be compared with energies $\varphi_i$ of unperturbed „dark" states, for example, with energies of composite vibrations (obertones).

## DW1-model Hamiltonian matrix

The basis of „dark" states can not be considered as fixed, therefore a form of recovered Hamiltonian matrix other than (2) is also possible. In particular, as mentioned above, it is proposed [24,28] to select from „dark" states only one single state coupled with the „bright" state. This selected state is known as doorway-state[1] (DW), and the essence of its singling out consists in that the corresponding dynamic problem assumes that after the „bright" state $\varphi_1$ is excited, further transitions to „dark" states are represented not as a set of $\varphi_1 \to \Phi_m$ transitions ($m = 2, 3, \ldots, n$) as in the direct-coupling model, but as a single transition responsible for $\varphi_1$ deactivation (without taking into account the $\varphi_1 \to \varphi_0$ reverse transition). This intermediate (the first) $|\mathrm{DW1}\rangle$-state, in turn becomes the initial state for transitions to further „dark" states. In the static problem, this model assumes that the $\varphi_0 \to |\mathrm{DW1}\rangle$ transition borrows a part of intensity from the transition to „bright" states, $\varphi_0 \to \varphi_1$, and then it itself becomes a source of intensity redistribution for transitions to other „dark" states; the latter are represented again in the form of direct-coupling model, which is a significant note. Below we shall show how we can get on from the direct-coupling model to DW-models with one state $|\mathrm{DW1}\rangle$, and then to models with a sequence of $|\mathrm{DW}\rangle$-states.

The proposed algorithm is composed of two stages. At the first stage an elementary step of Householder triangulation of symmetric real metrices is used (see [33], P. 218–219, 264–266), where similarity transformation $P^{-1}HP$ is applied to matrix (2) using reflection matrix $P$. Matrix $P$ is represented in a block form:

$$P = \begin{pmatrix} 1 & 0 \\ 0 & Q \end{pmatrix}, \tag{5}$$

where $(n-1) \times (n-1)$ matrix $Q$ is also a reflection matrix and is constructed of vector $V$ of size $n-1$: $Q = I - 2V \cdot V^t/(V^t V)$, $I$ is unity matrix, $V \cdot V^t$ is dyad matrix, $V^t V = \Sigma_{i=1}^{n-1} V_i^2$ is a scalar product that yields squared „length" of vector $V$. Reflection matrices $Q$ and $P$ are involutive,

$$Q^2 = I,\ P^2 = \begin{pmatrix} 1 & 0 \\ 0 & I \end{pmatrix},$$

saying that $Q^{-1} = Q$, $P^{-1} = P$, as well as $Q^t = Q$, $P^t = P$. Therefore $P^{-1}HP = PHP$.

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[1] Doorway means an aperture of door, the main entrance into a room, a portal.

Vector $V$ is defined in such a way that it differs from vector $B$ only by the $V_1$ component:

$$V_1 = B_1 - w_1, \quad V_i = B_i, \quad i = 2, 3, \ldots, n-1, \tag{6}$$

where

$$w_1 = -\mathrm{sgn}(B_1)(B^tB)^{1/2}, \quad B^tB = \Sigma_{i=1}^{n-1}B_i^2. \tag{7}$$

The similarity transformation $PHP$ results in that

$$PHP = \begin{pmatrix} 0 & (B-V)^t \\ B-V & QAQ \end{pmatrix},$$

$(PHP)_{11} = 0$ as before, and $(B-V)^t = (w_1, 0, \ldots, 0)$, i.e. all off-diagonal elements of the first column (as well as the first row) of the $PHP$ matrix are equal to zero, except for one:

$$(PHP)_{21} = (PHP)_{12} = w_1. \tag{8}$$

Elements of the $QAQ$ matrix ( $A$ is a diagonal matrix) are calculated by the following formula:

$$(QAQ)_{ij} = \delta_{ij}A_i - 2V_i(A_i - T + A_j - T)V_j/(V^tV), \tag{9}$$

where $T = \Sigma_{i=1}^{n-1}V_i^2A_i = V^tAV$. It would seem that according to (9) for an element of $(QAQ)_{11}$ a distinguished contribution from $A_1$ takes place, however, after transformation we get

$$(QAQ)_{11} = \Sigma_{i=1}^{n-1}B_i^2A_i/(B^tB) = B^tAB/(B^tB) \equiv g_1, \tag{10}$$

i.e. $g_1$ is defined by equitable contribution of all values, $A_i$ and $B_i$. Let us, in turn, represent the $QAQ$ matrix in a block form:

$$QAQ = \begin{pmatrix} g_1 & d^t \\ d & f \end{pmatrix}, \tag{11}$$

where vector $d$ of size $n-2$ and matrix $f$ of size $(n-2)\times(n-2)$ are defined by components $d_{i-1} = (QAQ)_{1i}$ and $f_{i-1,j-1} = (QAQ)_{ij}$ for $i, j = 2, 3, \ldots, n-1$.

The second step of the algorithm is implemented using direct-coupling model formulae, specifically, we shall formulate an eigenproblem for the $f$ matrix:

$$fz = za, \tag{12}$$

where $a = \mathrm{diag}(a_1, a_2, \ldots, a_{n-2})$, and form matrices

$$y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & z^t \end{pmatrix}$$

and $c = yP$. The latter is used to perform the similarity transformation from the direct-coupling model Hamiltonian matrix $H$ to the required DW1-model Hamiltonian matrix $H' = cHc^t$, or $H^{\mathrm{DW1}} \equiv cH^{\mathrm{DIR}}c^t$. The $H'$ matrix is diagonalized by matrix $C' = cC$, $H'C' = C'E$. The final block form of $H'$ is:

$$H' = \begin{pmatrix} 0 & w_1 & 0 \\ w_1 & g_1 & b^t \\ 0 & b & a \end{pmatrix}, \tag{13}$$

where components of vector $b$, as components of $B$ before, are calculated by the following formula:

$$b_p = \Sigma_{q=1}^{n-2}d_qz_{qp}, \quad p = 1, 2, \ldots, n-2. \tag{14}$$

In accordance with the similarity transformation $H' = cHc^t = (yP)H(yP)^t$, the transition is performed from basis functions of „dark“_ states $\Phi_m$ to their linear combinations: initially - to $\Phi_m = \Sigma_{m'=2}^{n}Q_{m'-1,m-1}\Phi_{m'}$, $(m = 2, 3, \ldots, n)$, then - to $\Phi'_2 = \Phi_2 \equiv |\mathrm{DW1}\rangle$ and $\Phi_m = \Sigma_{m'=3}^{n}z_{m-2,m'-2}\Phi_{m'}$, $(m = 3, 4, \ldots, n)$. Energy of the first DW1-state $H'_{22} = g_1$ is calculated by formula (10) as a weighed mean value of the energy of „dark“ states of direct-coupling model $A_i$ with weights $B_i^2/(B^tB)$, which is similar to calculation of the center of gravity of the observed conglomerate $G$ with normalized intensities $I'_k/\Sigma_{l=1}^{n}I'_l$. Due to the $H'_{12} = H'_{21} = w_1$ matrix element, the $|\mathrm{DW1}\rangle$ state borrows intensity from the „bright“ state, and due to $b_p$ matrix elements it, in turn, becomes a source of borrowing for the rest of „dark“ states, which energies $a_p$ are defined by the eigenproblem solution (12).

In the dynamic problem, in problems of non-radiative transitions or IVR, by assuming that after the absorption of a light quantum $\varphi_0 \to \varphi_1$ the $\varphi_1$ „bright“ state becomes populated, the rate constant of subsequent direct transitions $\varphi_1 \to \Phi_{i+1}$ in the direct-coupling model will be proportional to $(B_i)^2$, and the sum constant will be $\Sigma_{i=1}^{n-1}(B_i)^2$. In the DW1-model, there is only one transition of this kind, $\varphi_1 \to |\mathrm{DW1}\rangle$, and its rate constant is proportional to $(w_1)^2$, however $(w_1)^2 = \Sigma_{i=1}^{n-1}(B_i)^2$.

## Building up the Hamiltonian matrix of DW1-model directly from equation (3) for $XEX^t$

From point of view of transformation of a matrix to the tridiagonal form, its first step can be started not from the $H$ matrix in form (2), but from the $XEX^t$ matrix taking into account its block structure (3), and taking vector $D$ instead of vector $B$ as a basis in formulae (5)–(7). But since $D^tD = D^tZZ^tD = B^tB$, the relation of the „bright“ state with the DW1-state $\bar{w}_1$ will be the same, differing from the $w_1$, perhaps, by $\mathrm{sgn}(D_1)$ as compared to $\mathrm{sgn}(B_1)$, and $|\bar{w}_1| = |w_1|$. As for the energy of the $|\mathrm{DW1}\rangle$ state, it is calculated by the following formula: $\bar{g}_1 = D^tFD/(D^tD)$, but $D^tFD = D^tZAZ^tD = B^tAB$, and remains unchanged, $\bar{g}_1 = g_1$. After the appropriate similarity transformation of the block similar to the block $f$ in (11), the $XEX^t$ matrix takes the form of $H'$ matrix (13).

Thus, the Householder triangularization yields main parameters of the DW1-model: energy of the $|\mathrm{DW1}\rangle$-state $g_1$ and matrix element of its coupling with the „bright“ state $w_1$, that can be calculated directly from the $XEX^t$ matrix taking into account formula (3) or through the direct-coupling model:

$$g_1 = D^tFD/(D^tD) = B^tAB/(B^tB),$$

$$|w_1| = (D^t D)^{1/2} = (B^t B)^{1/2}. \tag{15}$$

In addition, since the matrix $XEX^t = X\mathrm{diag}(E_1, E_2, \dots, E_n)X^t$ is determined directly by the experimental data of $E_k$ and $I_k$, for $(w_1)^2$ and $g_1$ the following can be easily derived

$$(w_1)^2 = \Sigma_{k=1}^n E_k^2 I_k,$$

$$g_1 = \Sigma_{k=1}^n E_k^3 I_k / \Sigma_{l=1}^n E_l^2 I_l = \Sigma_{k=1}^n E_k^3 I_k/(w_1)^2, \tag{16}$$

i.e. they are determined from the distribution of square of $E_k^2$ and cube of $E_k^3$ of observed energies (relative to the center of gravity $G$) with weights of $I_k$. Formulae (16) coincide with the expressions obtained in [31].

It must be noted that square of the matrix element of the „bright“ state coupling with the $|\mathrm{DW1}\rangle$-state, $(w_1)^2$, remains invariant under orthogonal transformations of „dark“ states. This gives us the following equations:

$$(w_1)^2 = |\langle\varphi_1|\hat{H}^{(1)}|\mathrm{DW1}\rangle|^2 = \Sigma_{m=2}^n |\langle\varphi_1|\hat{H}^{(1)}|\Phi_m\rangle|^2$$

$$= \Sigma_{m=2}^n |\langle\varphi_1|\hat{H}^{(1)}|\varphi_m\rangle|^2. \tag{17}$$

The latter indicates that the rate constant of „bright“ state deactivation as a result of the $\varphi_1 \to |\mathrm{DW1}\rangle$ transition, which is proportional to $(w_1)^2$, as expected, is defined by the interaction of the „bright“ state with all zero-order „dark“ states $\varphi_m$, which are eigenfunctions of the Hamiltonian $\hat{H}^{(0)}$.

## Comparison with the method based on the Green's function

In the method developed in [25–27,31], that uses the formalism of the Green's function, solving the inverse problem of deconvolution in the direct-coupling model is reduced initially to determining roots of the following function:

$$f^{\mathrm{DIR}}(x) = \Sigma_{k=1}^n I_k/(E_k - x). \tag{18}$$

The $f^{\mathrm{DIR}}(x) = 0$ equation is solved numerically by the bisection method and yields values of $A_i$, $i = 1, 2, \dots, n-1$. At this, if we assume that the $\{E_k\}$ sequence is increasing, roots $A_i$ of equation (18) fall into the interval of $[E_i, E_{i+1}]$ and again form an increasing sequence $\{A_i\}$. Then, the square of matrix elements of coupling is calculated from the following equation:

$$B_i^2 = 1/\Big[\Sigma_{k=1}^n I_k/(E_k - A_i)^2\Big]. \tag{19}$$

The subsequent selection of the sign of matrix element $B_i$ is unessential.

When calculating parameters of the $H^{\mathrm{DW1}}$ Hamiltonian [31], once the values of $A_i$ and $B_i^2$ are determined, first of all the normalized squares of matrix elements of coupling are calculated: $J_i = B_i^2/\Sigma_{j=1}^{n-1} B_j^2$, which are interpreted as analogues of the observed normalized intensities $I_k$, and energies of „dark“ states $A_i$ — as analogues of the observed energies of transitions $E_k$. In accordance with this, a function similar to (18) is considered:

$$f^{\mathrm{DW}}(x) = \Sigma_{i=1}^{n-1} J_i/(A_i - x).$$

Roots $a_p$, $p = 1, 2, \dots, n-2$ of the $f^{\mathrm{DW}}(x) = 0$ equation, that fall into the interval of $[A_p, A_{p+1}]$, are determined numerically, and the square of matrix elements of coupling of the $|\mathrm{DW1}\rangle$ state and the rest of „dark“ states $b_p^2$ is calculated from the following equation:

$$b_p^2 = 1/\Big[\Sigma_{i=1}^{n-1} J_i/(A_i - a_p)^2\Big].$$

Parameter $g_1$ of the $H^{\mathrm{DW1}}$ Hamiltonian is calculated using formulae (10) or (16), and parameter $w_1$ is calculated with the help of (7) or (16).

Here the following note must be made. The classical approach in the problem of matrix diagonalization (for many quantum-mechanical problems — real, symmetrical) consists in that first its eigenvalues are determined, and then eigenvectors are derived (method eva → evc). However, even for $n \geq 3$ order matrices difficulties arise in determining the roots of characteristic polynomial. Therefore another approach has appeared to be practically important: first, on the basis of some methods (Jacobi rotations, *QR*-, *QL*-algorithms, methods of Givens, Householder, etc. [33]) the matrix of eigenvectors is determined, so that after the similarity transformation of the matrix in question it takes a diagonal form (method evc → eva). For the purpose of calculations the software implementation of the second method has became standard. From this point of view the method developed in [25–27,31] for the spectral deconvolution problem in question can be considered as analogue of the method eva → evc: first equation (18) is solved, followed by equation (19). In contrast to this, in our studies [15,32] the first step consists in building up an orthogonal matrix $X$ meeting the condition of $(X_{1k})^2 = I_k$. Further solving process is based first of all on formula (3), and in general our method is similar to evc → eva for both the direct-coupling model and the DW1-model.

## Hamiltonian matrices in the model with several DW-states

The block of the $(n-1) \times (n-1)$ matrix $H'$ in formula (13), resulted from the proceeding from the direct-coupling model to the DW1-model,

$$\begin{pmatrix} g_1 & b^t \\ b & a \end{pmatrix} \tag{20}$$

is completely analogous to form (2) of the $H$ matrix (the presence of $H'_{22} = g_1$ element, generally non-zero, is unessential). Therefore, the proceeding from the DW1-model to the DW2-model with two doorway-states can be implemented through the Householder triangularization of block (20) using formulae similar to (5)−(14), with

**Table 1.** Experimental data for acetylene molecule [14] (energy $E_k$ ($\mathrm{cm}^{-1}$) and normalized intensities $I_k$ of the „conglomerate“ of lines in the region of rotational component $R(2)$ ($G = 45307.1738\,\mathrm{cm}^{-1}$) of the electronic-vibrational transition $3_0^3K_0^1$ of the system $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ and calculated parameters of direct-coupling Hamiltonians $H^{\mathrm{DIR}}$ and doorway-models $H^{\mathrm{DW1}}$ and $H^{\mathrm{DW8}}$ ($\mathrm{cm}^{-1}$)

| Experimental data | | Parameters $H^{\mathrm{DIR}}$ | | | Parameters $H^{\mathrm{DW1}}$ | | Parameters $H^{\mathrm{DW8}}$ | |
|---|---|---|---|---|---|---|---|---|
| $E_1$–$E_9$ | $I_1$–$I_9$ | $A_1$–$A_8$ | $B_1$–$B_8$ | $B_1$–$B_8$ [14] | $g_1$ | $w_1$ | $g_1$–$g_8$ | $w_1$–$w_8$ |
| −0.1894 | 0.03 | | | | 0.0272 | −0.1188 | | |
| −0.1772 | 0.03 | −0.1864 | 0.0164 | 0.0168 | $a_1$–$a_7$ | $b_1$–$b_7$ | 0.0272 | −0.1188 |
| −0.1147 | 0.02 | −0.1722 | 0.0272 | 0.0310 | −0.1842 | −0.0155 | −0.0943 | 0.0636 |
| −0.0889 | 0.49 | −0.1137 | 0.0067 | 0.0064 | −0.1591 | −0.0528 | 0.0867 | 0.1256 |
| −0.0327 | 0.01 | −0.0341 | −0.0138 | 0.0137 | −0.1131 | 0.0114 | −0.0639 | 0.0383 |
| 0.1245 | 0.30 | 0.0378 | 0.1103 | 0.1080 | −0.0330 | −0.0097 | −0.0211 | 0.0765 |
| 0.1452 | 0.03 | 0.1432 | −0.0107 | 0.0104 | 0.1420 | 0.0132 | 0.0236 | −0.1323 |
| 0.1701 | 0.06 | 0.1635 | 0.0231 | 0.0235 | 0.1587 | −0.0243 | −0.0847 | −0.0598 |
| 0.1759 | 0.03 | 0.1746 | 0.0070 | 0.0070 | 0.1742 | −0.0057 | 0.1392 | −0.0788 |

the replacement of $A \rightarrow a$, $B \rightarrow b$. The Householder similarity transformation of block (20) will affect only „dark“ states $\Phi'_m$ at $m = 3, 4, \ldots, n$. Energy of the DW1-state $g_1$ and matrix element of its coupling with the „bright“ state $w_1$ will remain unchanged. As a result, for the key elements of the DW2-model Hamiltonian we get the energy of the DW2-state equal to $g_2 = b^tab/(b^tb)$ and the matrix element of its coupling with the DW1-state will be $w_2 = -\mathrm{sgn}(b_1)(b^tb)^{1/2}$.

In a similar way further proceeding with DW3-, DW4-, $\ldots$, DW$(n-2)$-models is implemented by successive steps, their maximum possible number is $n-2$, with no need to solve the equation for eigenvalues of form (12) at the last step. The Hamiltonian matrix of the DW$(n-2)$-model will be completely three-diagonal:

$$H^{\mathrm{DW}(n-1)} = \begin{pmatrix} 0 & w_1 & 0 & \ldots & 0 & 0 \\ w_1 & g_1 & w_2 & \ldots & 0 & 0 \\ 0 & w_2 & g_2 & \ldots & 0 & 0 \\ \hdotsfor{6} \\ 0 & 0 & 0 & \ldots & g_{n-2} & w_{n-1} \\ 0 & 0 & 0 & \ldots & w_{n-1} & g_{n-1} \end{pmatrix}. \quad (21)$$

Using the terminology of [24,28], one can say that the $H^{\mathrm{DW}(n-1)}$ matrix is defined in a so-called channel spectroscopic basis. For the dynamics of molecule after $\varphi_0 \rightarrow \varphi_1$ excitation actual transitions are initially from the „bright“ state to the first doorway-state, $\varphi_1 \rightarrow |\mathrm{DW1}\rangle$, and then successively between doorway-states: $|\mathrm{DW1}\rangle \rightarrow |\mathrm{DW2}\rangle \rightarrow \ldots \rightarrow |\mathrm{DW}(n-2)\rangle \rightarrow |\mathrm{DW}(n-1)\rangle$. Here it is worth to note that solving the time problem requires to take into consideration a host of other transitions: first - the reverse transitions of $\varphi_1 \rightarrow \varphi_0$, $|\mathrm{DW1}\rangle \rightarrow \varphi_1$, $|\mathrm{DW2}\rangle \rightarrow |\mathrm{DW1}\rangle \ldots |\mathrm{DW}(n-1)\rangle \rightarrow |\mathrm{DW}(n-2)\rangle$ type and second - the deactivation of „dark“ states, because „dark“ states may turn out to be „bright“ in relation to $|\mathrm{DWk}\rangle \rightarrow \chi$ transitions, where $\chi$ states are other than $\varphi_0$ [5]. Consideration of such a problem is beyond the scope of this work.

The direct coupling model together with DW1- and DW$(n-2)$-models is illustrated in Fig. 3.

## Numerical calculation of Hamiltonian matrix elements in doorway-models

The algorithm of proceeding from the direct-coupling model to DW-models on the basis of the above-presented formulae is implemented by us in the form of a Fortran program. With this program calculations were made for a number of molecular systems, where experimental data are represented quantitatively [9–12,14].

In particular, the acetylene molecule calculations of [14] use an extensive data for the „conglomerates“ of lines observed in rotational $Q$- and $R$- branches of the electronic-vibrational transitions $3_0^3K_0^1$ and $3_0^4K_0^1$ of the system $\tilde{A}^1A_u \leftarrow \tilde{A}^1\Sigma_g^+$. Table 1 presents, as an example, the results of parameter calculation of Hamiltonians for the direct-coupling model, $H^{\mathrm{DIR}}$, and doorway-models, $H^{\mathrm{DW1}}$ and $H^{\mathrm{DW8}}$, for the „conglomerate“ ($n = 9$) in the region of the rotational component $R(2)$ of the vibronic transition $3_0^3K_0^1$. As can be seen from Table 1, the increasing sequence $\{E_k\}$ ($k = 1, \ldots, n$) yields increasing sequences $\{A_i\}$ and $\{a_p\}$, so that values of $A_i$ fall into the interval of $[E_i, E_{i+1}]$ ($i = 1, \ldots, n-1$), and values of $a_p$ fall into the interval of $[A_p, A_{p+1}]$ ($p = 1, \ldots, n-2$). In addition, it should be noted that experimental energies $E_k$ are given in [14] with an accuracy of four decimal places, while intensities are given with an accuracy of two decimal places (for some „conglomerates“ of lines formally the equation of $\Sigma_{k=1}^n I_k = 1$ is not always fulfilled). Therefore, for the parameters of Hamiltonians listed in Table 1 with an accuracy of four decimal places at least one place should be considered excessive. This circumstance also can explain the difference in matrix elements of coupling $B_i$ in our

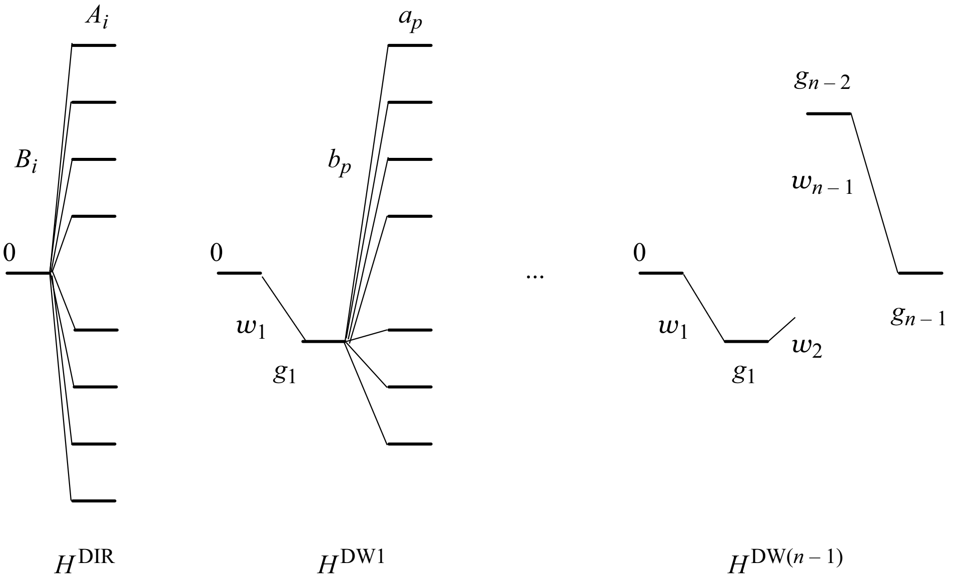

**Figure 3.** Diagrams of Hamiltonians of direct coupling model, DW1- and DW$(n-2)$-models.

**Table 2.** Parameters of Hamiltonian $H^{\mathrm{DW1}}$ (in cm$^{-1}$) of spectral deconvolution for the „conglomerate“ of components of rotational $Q$- and $R$-branches of electronic-vibrational transitions $3_0^3K_0^1$ and $3_0^4K_0^1$ of the system $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ of acetylene molecule calculated from the experimental data of [14]: $g_1$ — energy of the $|\mathrm{DW1}\rangle$ state, $w_1$ — matrix element of its coupling with the „bright“ state, $G$ — energy of the „bright“ state (in relation to the ground state)

| Component | $G$ | $g_1$ | $g_1$ [31] | $w_1$ | $w_1$ [31] |
|---|---|---|---|---|---|
| | | | $3_0^3K_0^1$ | | |
| $R(0)$ | 45303.1255 | −0.2730 | −0.2731 | −0.1418 | 0.1418 |
| $R(1)$ | 45305.2209 | −0.1120 | −0.1120 | −0.1206 | 0.1206 |
| $R(2)$ | 45307.1738 | 0.0273 | 0.0272 | −0.1188 | 0.1188 |
| $R(3)$ | 45308.9132 | 0.0990 | 0.0990 | −0.1704 | 0.1704 |
| $Q(1)$ | 45300.6503 | 0.0418 | 0.0418 | −0.1980 | 0.1980 |
| $Q(2)$ | 45300.1678 | −0.0508 | −0.0508 | −0.1245 | 0.1245 |
| $Q(3)$ | 45299.4414 | −0.2272 | −0.2272 | −0.1784 | 0.1785 |
| $Q(4)$ | 45298.4825 | −0.1753 | −0.1753 | −0.1695 | 0.1695 |
| | | | $3_0^4K_0^1$ | | |
| $R(0)$ | 46290.4644 | 0.0336 | | −0.1051 | |
| $R(1)$ | 46292.5043 | −0.0794 | | −0.0547 | |
| $R(2)$ | 46294.3631 | 0.1412 | | −0.0883 | |
| $R(3)$ | 46296.0968 | 0.1878 | | −0.1222 | |
| $Q(1)$ | 46287.9946 | 0.0521 | | −0.0883 | |
| $Q(2)$ | 46287.5005 | −0.1668 | | −0.0977 | |
| $Q(3)$ | 46286.7643 | 0.0495 | | −0.1089 | |
| $Q(4)$ | 46285.5968 | −0.0283 | | −0.0240 | |

calculations and in calculations of [14], probably made with a greater accuracy of intensity values $I_k$. The experimental data $\{E_k\}$, $\{I_k\}$ of [14] were also used in [31] to calculate Hamiltonian parameters for the DW1-model on the basis of the Green's function. As can be seen from Table 2, for the „conglomerates“ of transition lines our calculation and calculation of [31] lead to the same result.

## Conclusion

Main results of this study can be summarized as follows. The initial point for building up models of spectral deconvolution for the complex Fermi resonance or its vibronic analogue is the $XEX^t$ matrix, where $E = \mathrm{diag}(\{E_k\})$ is a diagonal matrix composed of energies of the observed „conglomerate“ of lines, and intensities of these lines define the first row of the matrix $X$, $(X_{1k})^2 = I_k$, $k = 1, 2, \ldots, n$. The Hamiltonian matrix of the direct-coupling model, $H^{\mathrm{DIR}}$, which parameters are $A_i$ — energy of „dark“ states and $B_i$ — matrix elements of their interaction with the „bright“ state, $(i = 1, 2, \ldots, n-1)$, is derived after diagonalization of the $XEX^t$ block referred to „dark“ states. The use of Householder triangularization method, where reflection matrices are constructed from vectors $B$ or $D$ $(D_i = (XEX^t)_{1,i+1})$, allows proceeding from $H^{\mathrm{DIR}}$ or $XEX^t$ matrices to the Hamiltonian matrix of the doorway-model with one DW1-state, $H^{\mathrm{DW1}}$. Expressions are obtained for the energy of the first doorway-state and the matrix element of its coupling with the „bright“ state:

$$g_1 = \Sigma_{i=1}^{n-1} B_i^2 A_i \Big/ \left(\Sigma_{j=1}^{n-1} B_j^2\right) = \Sigma_{k=1}^{n} E_k^3 I_k / \Sigma_{l=1}^{n} E_l^2 I_l,$$

$$|w_1| = \left(\Sigma_{i=1}^{n-1} B_i^2\right)^{1/2} = \left(\Sigma_{k=1}^{n} E_k^2 I_k\right)^{1/2}.$$

In a similar way, using the Householder method the proceeding to the Hamiltonian matrices with several DW-states: $H^{\mathrm{DW2}}, \ldots, H^{\mathrm{DW}(n-1)}$ is implemented successively. The Hamiltonian of the DW$(n-2)$-model is represented by a symmetrical three-diagonal matrix

$H^{\mathrm{DW}(n-1)}$, its diagonal elements $g_i$ define the energies of DW1-, DW2-, …, DW$(n-1)$-states, while non-diagonal elements $w_i$ define the successive coupling between them.

It should be emphasized that Hamiltonian matrices of the direct-coupling model and the DW-models are related to each other by a similarity transformation, because of which the $H^{\mathrm{DIR}}, H^{\mathrm{DW1}}, H^{\mathrm{DW2}}, \ldots, H^{\mathrm{DW}(n-1)}$ Hamiltonians should be considered as equivalent. Hamiltonians of DW-models are defined in bases corresponding to different linear combinations of „dark" states $\Phi_m$ of the direct-coupling model. However, the $\Phi_m$ basis is related to the basis of zero-order approximation functions $\varphi_m$ with a clear physical meaning only by an implicit pre-diagonalization. In general, in the inverse problem for the complex Fermi resonance or its vibronic analogue, to recover the Hamiltonian matrix in the unique form a total of $n(n+1)/2-1$ parameters are needed, but at $n \geq 3$ this number exceeds $2n-2$ independent experimental values $\{E_k\}$ and $\{I_k\}$. To select between the models under consideration, an additional information is required along with the data of $\{E_k\}$ and $\{I_k\}$.

The obtained results can be used in the consideration of dynamic problems, which are actual, in particular, for the problem of non-radiative transitions in polyatomic molecules and intramolecular redistribution of vibrational energy [7]. The evident advantage of models with many doorway-states for solving the time problem consists in that they assume successive propagation of the excitation along the chain of „dark" states, and the initial transition from the „bright" state is the only one, $\varphi_1 \to |\mathrm{DW1}\rangle$. The direct-coupling model initially requires to take into account all the $\varphi_1 \to \Phi_m$ transitions at once. Initially the calculations of dynamics could be conducted if only $w_1$ and $g_1$ parameters of the $H^{\mathrm{DW1}}$ Hamiltonian are taken into account (they should be taken from the spectral deconvolution for the specific spectrum) together with the variable rate constant of the irreversible process $|\mathrm{DW1}\rangle \to \chi$ (the $\chi$ state is other than $\varphi_0$ [5]). The model of this kind was considered in [34]. Among the results of this study, it is worth to note the oscillating dependence (quantum beats) of population of the states in question, which develops on the background of exponential decrease related to the transitions similar to $|\mathrm{DW1}\rangle \to \chi$. Subsequent calculations could be complicated by taking into account parameters of the $|\mathrm{DW2}\rangle$-state, $w_2$ and $g_2$, the $|\mathrm{DW2}\rangle \to \chi'$ transition, etc. It must be noted that quantum beats were observed experimentally for the molecule of pyrazine [11,12].

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