

Dressed basis for highly excited molecular vibrations

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Starting from a multiresonance spectroscopic Hamiltonian fit by Baggott to experimental levels of H₂O, an approximate Hamiltonian is devised using a prediagonalized “dressed” zero-order basis, within which a residual, effective single-resonance coupling operator acts. The dressed basis incorporates many of the effects of nonintegrability, while the effective resonance furnishes much of the simplicity of integrable systems. Numerical tests are performed for two distinct dressed bases, in which different resonance operators are chosen as the residual effective coupling. Excellent agreement with the energies and eigenvectors of the exact system is obtained for each of the two dressed bases. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569908]

I. INTRODUCTION

In this paper, we investigate a “dressed basis” method in which a many-mode, multiresonance spectroscopic Hamiltonian is approximated by a Hamiltonian with a new zero-order basis, within which there acts a residual effective single-resonance coupling operator. The dressed zero-order basis is prediagonalized with a portion of the original spectroscopic Hamiltonian. The dressed basis is intended to incorporate many of the effects of nonintegrability, while the single effective resonance furnishes much of the simplicity of an integrable system.

This is motivated by certain results of investigations of highly excited molecular vibrations. In a series of papers,^{1–17} we have been developing bifurcation analysis^{5,6} of the Hamiltonian corresponding semiclassically to the spectroscopic quantum fitting Hamiltonian. This identifies the anharmonic modes, born in bifurcations of the original (3*N* – 6) low-energy normal modes, that characterize the molecule at high energy. This kind of procedure, now applied by a number of authors,^{18–32} started with simple two-mode systems with a single Fermi resonance coupling, but has been successfully extended to more than two modes with multiple resonances and chaos.^{11,12,15,23,24,28}

One of the most salient findings¹² has been that the bifurcations of most molecules can be decomposed into a sequence of independent two-mode bifurcations, similar, despite the nonintegrability and chaos of the system, to those observed for systems of a single resonance between two modes. The dressed basis is a computational method that mirrors this approximate classical decomposability into systems of quasi-independent resonances. The dressed basis method is not difficult to apply and may find use as a practical tool, as briefly described in the concluding section.

II. DRESSED BASIS SETS AND EFFECTIVE RESONANCE

The observed decomposability into effective single-resonance systems suggests a systematic collection of ap-

proximations to the Hamiltonian, in each of which the system is viewed from the perspective of one of the independent resonances. In each approximate Hamiltonian, corresponding to a chosen resonance coupling V_i of the original Hamiltonian, there will be an effective resonance coupling V_i^{eff} . This will act within a zero-order basis which incorporates the effects of the rest of the original Hamiltonian, including both its zero-order part and all the other resonances besides V_i —hence, a “dressed” basis. The effective individual resonance operator V_i^{eff} will be defined so as to act within “sequences” of this basis.

For this to work, it is necessary to label the zero-order sequences with a set of N numbers that function like zero-order quantum numbers. At best, these will be effective or nominal quantum numbers, because they certainly cannot be true constants of motion of the dressed zero-order basis, which has a nonseparable Hamiltonian. But if this much can be made to work, we will have an effective Hamiltonian with nonintegrability via the dressed basis, but retaining as much as possible the simplicity of a single resonance approximation via the effective resonance V_i^{eff} . This procedure will be useful to the extent that the exact eigenstates of the spectroscopic Hamiltonian are approximated by those of the new effective Hamiltonian. Detailed construction and testing of dressed basis sets will be presented in Sec. V and following, after some useful preliminaries concerning the spectroscopic Hamiltonian and its structure.

III. SPECTROSCOPIC HAMILTONIAN

This section describes the spectroscopic Hamiltonian in sufficient detail for the later discussion of the dressed basis sets.

The Hamiltonian is a spectroscopic fitting Hamiltonian for a bent triatomic, with parameters optimized by Baggott³³ to give the best match to available data for H₂O. In the normal modes representation, the form of the Hamiltonian is

$$H^N = H_0^N + V_{DD}^N + V_F^N. \quad (1)$$

H_0^N is a zero-order Hamiltonian diagonal in normal-mode quantum numbers n_s , n_a , and n_b for symmetric stretch, an-

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tisymmetric stretch, and bend. The couplings V_{DD}^N and V_F^N are resonance terms between the normal modes. V_{DD}^N is a Darling–Dennison coupling³⁴ between the symmetric and antisymmetric stretch, and V_F^N is a 2:1 Fermi resonance coupling between the symmetric stretch and bend. This Hamiltonian is block diagonal in sets of the same total or polyad quantum number $P = n_s + n_a + n_b/2$.

In this paper, we will actually work in a representation with local O–H bond mode stretches, rather than the normal stretch modes of the representation of Eq. (1). The transformation between normal and local representations of the three-mode Hamiltonian (1) with bend has been carried out by Baggott.³³ After this transformation, in which the designation of the bend remains unchanged, the Hamiltonian becomes

$$H^L = H_0^L + V_{1:1}^L + V_{2:2}^L + V_{2:1}^L, \quad (2)$$

where

$$\begin{aligned} H_0^L = & \omega_0 \left(n_1 + \frac{1}{2} \right) + \omega_0 \left(n_2 + \frac{1}{2} \right) + \omega_b \left(n_b + \frac{1}{2} \right) \\ & + \alpha_s \left(n_1 + \frac{1}{2} \right)^2 + \alpha_s \left(n_2 + \frac{1}{2} \right)^2 + \alpha_b \left(n_b + \frac{1}{2} \right)^2 \\ & + \alpha_{ss} \left(n_1 + \frac{1}{2} \right) \left(n_2 + \frac{1}{2} \right) + \alpha_{sb} \left(n_1 + \frac{1}{2} \right) \left(n_b + \frac{1}{2} \right) \\ & + \alpha_{sb} \left(n_2 + \frac{1}{2} \right) \left(n_b + \frac{1}{2} \right), \end{aligned} \quad (3)$$

$$V_{1:1}^L = \left[\lambda + \lambda' (n_1 + n_2 + 1) + \lambda'' \left(n_b + \frac{1}{2} \right) \right] (a_1 a_2^\dagger + a_2 a_1^\dagger), \quad (4)$$

$$V_{2:2}^L = \gamma (a_1 a_1^\dagger a_2^\dagger a_2^\dagger + a_2 a_2^\dagger a_1^\dagger a_1^\dagger), \quad (5)$$

and

$$V_{2:1}^L = \frac{Q_{sbb}}{2\sqrt{2}} (a_1 a_b^\dagger a_b^\dagger + a_b a_b a_1^\dagger + a_2 a_b^\dagger a_b^\dagger + a_b a_b a_2^\dagger). \quad (6)$$

Here n_1 and n_2 refer to the number of quanta in the local O–H stretch modes and n_b to the number of quanta in the bend mode. $V_{1:1}^L$ is the 1:1 coupling between the local stretches. It is primarily responsible for the coupling that gives normal modes. The 2:2 coupling $V_{2:2}^L$ arises in the transformation from the normal to local representation^{1,3,35} of the Darling–Dennison Hamiltonian. Typically, it is small for stretches. The values for the normal-mode and local-mode spectroscopic constants for H₂O are given in Ref. 33. Both stretch–stretch couplings $V_{1:1}^L$ and $V_{2:2}^L$ act within sets of zero-order states with bend quantum number n_b constant, so we can combine them into a single stretch–stretch coupling

$$V_{SS}^L = V_{1:1}^L + V_{2:2}^L. \quad (7)$$

The structure of the couplings in the Hamiltonian leads naturally to schemes of zero-order sequences or subpolyads that will be useful later in defining the dressed basis sets. Polyad $P=8$ is shown schematically in Fig. 1. The zero-order basis states are labeled with their quantum numbers

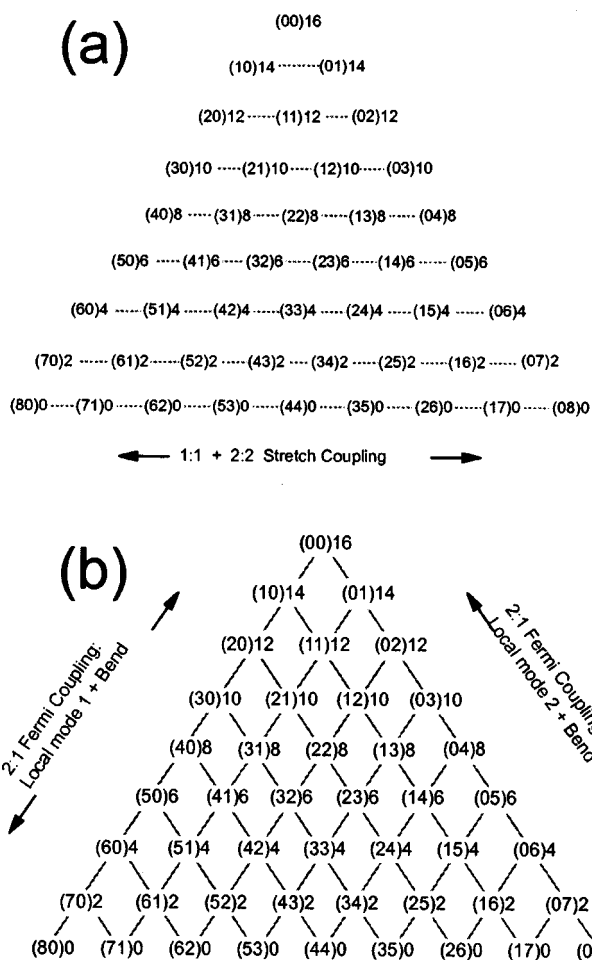


FIG. 1. Coupling and subpolyad structure of the zero-order spectrum, described in Sec. III and Ref. 13. Zero-order states are labeled by the quantum numbers $(n_1, n_2)n_b$. (a) Structure of the stretch–stretch coupling, (b) structure of the stretch–bend coupling.

$(n_1, n_2)n_b$. In the local representation, the coupling V_{SS}^L acts within zero-order local mode stretch–stretch subpolyads, as shown schematically in Fig. 1(a). It links sequences obtained as subpolyads or “slices” of the zero-order polyad. The stretch–bend coupling $V_{2:1}^L$ is more complicated. As seen from Eq. (6), by symmetry there actually are two stretch–bend Fermi couplings in the local representation, so the action of the couplings does not divide neatly into independent slices. Rather, the structure is the “net” depicted in Fig. 1(b).

IV. FAILURE OF THE ZERO-ORDER INDEPENDENT-RESONANCE APPROXIMATIONS AND THE NEED FOR THE DRESSED BASIS

Next, in the course of introducing some notation that will be useful later, we establish that the individual zero-order resonances are nowhere near an adequate approximation to the spectrum and eigenvectors of the full multiresonance Hamiltonian.

We have examined energy levels and eigenvector overlaps of each of four possible independent resonance approximations. [We call these “independent”- rather than “single”-resonance approximations, because of the two-

resonance net structure of the stretch-bend Fermi interaction in the local representation seen in Fig. 1(b)]. The four approximate Hamiltonians are

$$H_F^L = H_0^L + V_F^L, \quad (8)$$

$$H_F^N = H_0^N + V_F^N, \quad (9)$$

with stretch–bend coupling, and

$$H_{SS}^L = H_0^L + V_{SS}^L, \quad (10)$$

$$H_{DD}^N = H_0^N + V_{DD}^N, \quad (11)$$

with stretch–stretch coupling. The last two Hamiltonians actually are completely equivalent, being different representations of the same Hamiltonian, as described in Refs. 1 and 3. All four Hamiltonians (8)–(11) are listed because potentially each is associated with the construction of a distinct dressed basis Hamiltonian, as will become clear shortly.

As expected, we found that all four independent-resonance approximations give results, for the energies and especially the eigenvectors, that are poor for many of the levels. While each of the simple Hamiltonians (8)–(11) gives reasonable results for some levels, none gives good results for all portions of the spectrum. This is not surprising, because multiple-resonance couplings generally are added to a spectroscopic Hamiltonian only when they become necessary to account for the experimental data.

V. CONSTRUCTING AND TESTING THE DRESSED BASES

We now describe the various dressed basis sets and effective independent-resonance operators. Our goal is to devise approximations to the full Hamiltonian H^{full} which are simple, in the sense of being analogs of the zero-order independent-resonance Hamiltonians

$$H_\alpha = H_0 + V_\alpha \quad (12)$$

of Eqs. (8)–(11), yet which capture as much as possible the complexity of the nonintegrable, multiresonance Hamiltonian H^{full} . In analogy to the naive zero-order resonance Hamiltonians H_α of the previous section, we will refer to these various dressed Hamiltonians as H_α^{dr} .

We chose to work from the local mode form of the Hamiltonian (2) because the Fermi coupling happens to come into play strongly in polyad 8 for states where the stretch dynamics are best described by local modes. We have therefore investigated two different dressed basis Hamiltonians, which we now describe as methods 1 and 2, which are analogous to the two naive independent-resonance Hamiltonians Eqs. (8) and (10).

Each dressed Hamiltonian will take the form of a dressed zero-order Hamiltonian $H_{0\alpha}^{dr}$ plus a residual, effective independent-resonance coupling V_α^{eff} . The task is to give explicit formulation to the dressed zero-order Hamiltonian and the residual independent resonance. In general, the dressed zero-order Hamiltonian $H_{0\alpha}^{dr}$ will be defined as a sum of the zero-order Hamiltonian H_0 plus all the zero-order resonances V_i except the V_α intended to be replaced by the residual V_α^{eff} :

$$H_{0\alpha}^{dr} = H_0 + \sum_{i \neq \alpha} V_i. \quad (13)$$

The eigenstates of $H_{0\alpha}^{dr}$ give a dressed zero-order basis. This basis, in analogy to its counterpart H_0 , will be assigned a set of N nominal or effective zero-order quantum numbers. How this key step is to be performed will be specified later in each case with great care; it is emphatically *not* just a matter of taking overlaps of the dressed basis states with the states of the zero-order H_0 . In terms of these N labels, zero-order sequences or subpolyads are defined within which a given V_α^{eff} acts. Unlike the case with the original zero-order basis, the N quantum numbers are rightly called “nominal.” This is because the new zero-order states are dressed by all the other resonances of the spectroscopic Hamiltonian, so the nominal quantum numbers do not correspond to classical constants rigorously obtainable in any way of which we are aware; at best, they are approximate effective quantum numbers.

As in Refs. 11 and 13, for numerical testing we focus in detail on the polyad $P=8$ and just briefly summarize lower polyads (where the results are as good or better). We chose $P=8$ in Refs. 11 and 13 because it is in the region where both resonances come strongly into play.

A. Method 1: Dressed local stretch modes with effective stretch–bend resonance

The first Hamiltonian, by analogy to the naive independent resonance approximation (8), has a dressed zero-order basis of local stretches, with an effective residual stretch–bend Fermi coupling:

$$H_F^{L, dr} = H_{0F}^{L, dr} + V_F^{L, eff}. \quad (14)$$

The problem is to specify (1) how $H_{0F}^{L, dr}$ is defined with its dressed basis, (2) how the basis is assigned nominal zero-order quantum numbers, and (3) how matrix elements of $V_F^{L, eff}$ are defined in terms of the nominal quantum numbers.

Following the general form (13), we define $H_{0F}^{L, dr}$ as

$$H_{0F}^{L, dr} = H_0^L + V_{SS}^L. \quad (15)$$

That is, the original local stretches of H_0^L are dressed by $V_{SS}^L = V_{1:1}^L + V_{2:2}^L$ of Eq. (7), the stretch–stretch coupling in the local basis.

The next step is to assign nominal zero-order local-mode quantum numbers to the basis of the dressed zero-order Hamiltonian $H_{0F}^{L, dr}$. This is the most problematic aspect of our investigation, because there is no question of the nominal quantum numbers actually being rigorous constants for the basis states. We will work in each case by describing the actual procedure and the rationale for its use. While the nominal assignment procedures certainly do not have a rigorous justification, numerically their success far exceeds expectations, lending confidence that the basic idea is on the right track. It should be mentioned that the procedures for assigning nominal quantum numbers that will be described here are closely related to methods for assigning quantum numbers to spectra using diabatic correlation diagrams. These were developed by Rose and Kellman¹³ for H_2O , then applied^{36–38} to the more complex C_2H_2 system.

We now describe the detailed procedure followed in method 1. The dressed zero-order Hamiltonian $H_{0F}^{L, dr}$ contains the stretch–stretch coupling V_{SS}^L , and though its eigenstates have fixed bend quantum number n_b , they are strong mixtures of the original zero-order basis of H_0^L . In fact, from previous resonance analysis of coupled stretches,^{1,3,5,6} we know that they do not all retain local-stretch-mode character. Within a sequence with fixed n_b , the lower states have local-mode character and fall into near-degenerate local mode doublets, while the upper levels have normal-mode character. This mixture of two dynamical classes induced within the subpolyad by the coupling is the essential difficulty. Classically, there is a separatrix between local- and normal-mode regions in phase space. It is therefore not possible rigorously to assign a single set of stretch quantum numbers to all the states. We nonetheless will assign a single set of nominal zero-order quantum numbers $(n_1, n_2, n_b)^{nom}$. We do this by a diabatic correlation diagram technique similar to the procedure used in Ref. 13. For example, consider the sequence of dressed states with fixed $n_b=0$. The original zero-order states have good quantum numbers $(n_1, n_2, 0)^\pm$. When the coupling V_{SS}^L is turned on to give the dressed basis, we follow the zero-order states $(8,0,0)^\pm, (7,1,0)^\pm, \dots, (4,4,0)^\pm$ adiabatically as they are carried over to the states that we label $(8,0,0)^{\pm nom}, (7,1,0)^{\pm nom}, \dots, (4,4,0)^{\pm nom}$. (It turns out in the present case that the nominal quantum numbers assigned in this way preserve the original energy ordering.) Intuitively, it is plausible that the character of the states may not change too much in the diabatic correlation, so that the nominal zero-order assignments possess a physical meaning, roughly, of a bend mode being coupled to a stretching motion with about twice the frequency of the bend, with not too great a consequence from the precise nature, normal or local, of the stretching. Everything hinges on whether this leads to an effective Hamiltonian with a V^{eff} , such that its matrix structure and values of the matrix elements mimic the starting Hamiltonian. Proof for this will rest on numerical testing.

The final step is then to define matrix elements of this $V_F^{L, eff}$. This is very straightforward. By analogy with Eq. (6), we take $V_F^{L, eff}$ to be of the form

$$V_{2:1}^{L, eff} = \frac{Q_{sbb}^{L, eff}}{2\sqrt{2}} (a_1 a_b^\dagger a_b^\dagger + a_b a_b a_1^\dagger + a_2 a_b^\dagger a_b^\dagger + a_b a_b a_2^\dagger), \quad (16)$$

where the operators a_i and a_i^\dagger now have the action of raising and lowering operators on the *dressed* basis, with matrix elements determined by the nominal zero-order quantum numbers and the strength $Q_{sbb}^{L, eff}/2\sqrt{2}$ of the effective coupling—e.g.,

$$\begin{aligned} \langle (n_1 - 1), n_2, (n_b + 2) | V_F^{L, eff} | n_1, n_2, n_b \rangle^{nom} \\ = \frac{Q_{sbb}^{L, eff}}{2\sqrt{2}} \sqrt{n_1(n_b + 1)(n_b + 2)^{nom}}. \end{aligned} \quad (17)$$

We need to choose the strength of $Q_{sbb}^{L, eff}$. One could try to optimize this, but in this test we choose simply to use the values from the starting Hamiltonian of Eqs. (2)–(6); i.e., we take $Q_{sbb}^{L, eff} = Q_{sbb}$.

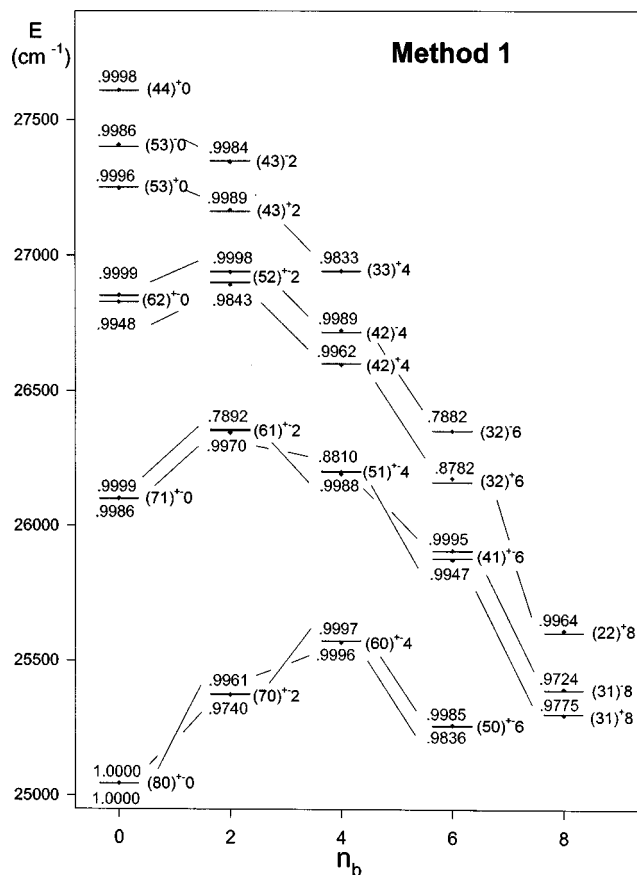


FIG. 2. Results of method 1 for energies and eigenvectors, as described in Sec. V A; see Table I for complete results for the $P=8$ polyad. The horizontal lines are exact energies; the diamonds are energies of the effective Hamiltonian $H_F^{L, dr}$ of method 1. Next to each level is given its nominal effective quantum number assignment, from Table I. The overlap of the eigenvector of the effective Hamiltonian with the exact eigenvector is given with each level. The “arches” of levels connected by angled lines are subpolyads or sequences of the stretch–bend Fermi resonance, described in Sec. VI B.

1. Results of method 1

Figure 2 and Table I show the results of method 1. The spectrum and overlaps of eigenvectors of the effective Hamiltonian are compared with the those of H^{full} . The horizontal levels in Fig. 2 give the energies of the exact eigenstates of H^{full} . The diamond symbols in Fig. 2 are the energies of the eigenstates of $H_F^{L, dr}$. In all cases, the approximate and exact energies are very close. The overlaps of the $H_F^{L, dr}$ eigenvectors with the exact vectors of H^{full} are given adjacent to each level. For the most part, there is remarkably good agreement, with overlaps above 0.97, and often much better, in all but four exceptional cases. Apart from these exceptional cases, the numerical results justify the hypothesis that the exact system can be mimicked by the effective Hamiltonian $H_F^{L, dr}$ with nominal assignments of the dressed zero-order basis and residual effective resonance. We now examine the reason and cure for the exceptional cases.

2. Mixing of accidental near degeneracies and dynamical tunneling

The worst cases in Fig. 2 are the pair $(6,1)^-2$ and $(3,2)^-6$, with overlaps with the corresponding exact eigen-

TABLE I. Results of the dressed basis Hamiltonians, described in Sec. V. Upper section, exact and approximate levels by methods 1 and 2. Under “ H^{full} ” are exact levels of H^{full} . The quantum number assignments $(n_1, n_2)^{\pm} n_b$ are obtained by continuing the diabatic assignments of the dressed basis to the complete Hamiltonian H^{full} ; this is the method of effective nominal quantum numbers used by Rose and Kellman for the full Hamiltonian in Fig. 8, right of Ref. 13. Under “Methods 1 and 2” are approximate energies of the corresponding levels for each method and overlaps of approximate and exact eigenvectors. Pairs of levels marked by letters a–f were subjected to 2×2 corrections in methods 1 and 2. In lower section, results for 2×2 corrections are summarized. Exact levels are in left bottom section; results for energies and overlaps of the corresponding approximate states after 2×2 corrections to methods 1 and 2 are given in the next two sections to the right.

H^{full} (level)	Energy	Assignment	Method 1		Method 2		
			Energy	Overlap	Energy	Overlap	
1	20945.50	(00) ⁺ 16	20961.67	0.9990	20946.74	1.0000	
2	22248.09	(10) ⁺ 14	22247.81	0.9971	22300.63	0.9999	
3	22344.96	(10) ⁻ 14	22344.98	1.0000	22294.70	1.0000	
4	23364.61	(20) ⁺ 12	23361.36	0.9977	23362.16	0.9997	
5	23410.02	(20) ⁻ 12	23412.42	0.9995	23409.25	0.9999	
6	23602.73	(11) ⁺ 12	23615.07	0.9985	23609.14	0.9997	
7	24256.23	(30) ⁺ 10	24252.77	0.9978	24262.22	0.9964	
8	24267.71	(30) ⁻ 10	24267.83	0.9995	24261.59	0.9985	
9	24525.49	(21) ⁺ 10	24529.09	0.9955	24611.61	0.9962	
10	24682.45	(21) ⁻ 10	24681.55	0.9987	24600.71	0.9983	
11	24894.53	(40) ⁺ 8	24892.63	0.9973	24893.41	0.9996	
12	24896.15	(40) ⁻ 8	24895.54	0.9988	24895.11	0.9995	
13	25044.66	(80) ⁺ 0	25044.93	1.0000	25044.96	0.9999	
14	25044.66	(80) ⁻ 0	25044.93	1.0000	25044.96	0.9999	
15	25258.10	(50) ⁺ 6	25260.73	0.9836	25260.35	0.9786	a
16	25259.35	(50) ⁻ 6	25261.11	0.9985	25260.69	0.9958	
17	25302.96	(31) ⁺ 8	25298.34	0.9775	25298.85	0.9756	a
18	25373.53	(70) ⁻ 2	25372.12	0.9740	25374.15	0.9737	b
19	25374.64	(70) ⁺ 2	25371.96	0.9961	25374.15	0.9899	
20	25391.17	(31) ⁻ 8	25395.41	0.9724	25387.50	0.9767	b
21	25573.86	(60) ⁺ 4	25566.69	0.9996	25565.03	0.9918	
22	25573.93	(60) ⁻ 4	25566.79	0.9997	25565.05	0.9917	
23	25603.72	(22) ⁺ 8	25611.34	0.9964	25616.39	0.9985	
24	25877.82	(41) ⁺ 6	25871.54	0.9947	25893.18	0.9859	
25	25905.59	(41) ⁻ 6	25906.83	0.9995	25890.67	0.9895	
26	26099.67	(71) ⁺ 0	26100.51	0.9986	26100.94	0.9943	
27	26100.17	(71) ⁻ 0	26100.87	0.9999	26100.99	0.9979	
28	26159.58	(32) ⁺ 6	26173.19	0.8782	26268.51	0.9318	c
29	26198.24	(51) ⁻ 4	26197.68	0.9988	26197.88	0.9641	
30	26200.60	(51) ⁺ 4	26190.50	0.8810	26193.29	0.9337	c
31	26350.20	(32) ⁻ 6	26350.07	0.7882	26254.51	0.7562	d
32	26351.11	(61) ⁺ 2	26343.63	0.9970	26346.27	0.9797	
33	26356.02	(61) ⁻ 2	26347.38	0.7892	26346.24	0.7644	d
34	26599.90	(42) ⁺ 4	26596.25	0.9962	26596.62	0.9851	
35	26714.96	(42) ⁻ 4	26721.59	0.9989	26709.46	0.9902	
36	26828.04	(62) ⁺ 0	26827.04	0.9948	26841.84	0.9156	e
37	26851.47	(62) ⁻ 0	26852.52	0.9999	26849.47	0.9835	
38	26898.70	(52) ⁺ 2	26890.60	0.9843	26914.20	0.9077	e
39	26939.37	(52) ⁻ 2	26937.49	0.9998	26911.77	0.9680	
40	26940.75	(33) ⁺ 4	26940.91	0.9833	26956.30	0.9685	
41	27161.25	(43) ⁺ 2	27166.28	0.9989	27269.83	0.9304	
42	27251.26	(53) ⁺ 0	27248.09	0.9996	27251.31	0.9445	
43	27346.97	(43) ⁻ 2	27343.82	0.9984	27255.11	0.8776	f
44	27399.93	(53) ⁻ 0	27405.93	0.9986	27371.84	0.8995	f
45	27608.05	(44) ⁺ 0	27608.91	0.9998	27619.13	0.9975	
			Method 1 corrected		Method 2 corrected		
15	25258.10	(50) ⁺ 6	25258.04	0.9994	25260.26	0.9985	a
17	25302.96	(31) ⁺ 8	25302.67	0.9932	25304.05	0.9954	a
18	25373.53	(70) ⁻ 2	25373.51	0.9997	25381.46	0.9598	b
20	25391.17	(31) ⁻ 8	25391.70	0.9979	25392.05	0.9614	b
28	26159.58	(32) ⁺ 6	26161.06	0.9957	26154.96	0.9878	c
30	26200.60	(51) ⁺ 4	26201.09	0.9973	26193.69	0.9889	c
31	26350.20	(32) ⁻ 6	26350.10	0.9963	26340.68	0.8628	d
33	26356.02	(61) ⁻ 2	26355.41	0.9964	26353.04	0.8684	d
36	26828.04	(62) ⁺ 0			26854.37	0.9333	e
38	26898.70	(52) ⁺ 2	26898.22	0.9975	26913.42	0.9282	e
40	26940.75	(33) ⁺ 4	26939.11	0.9958			
43	27346.97	(43) ⁻ 2			27317.98	0.9662	f
44	27399.93	(53) ⁻ 0			27391.16	0.9920	f

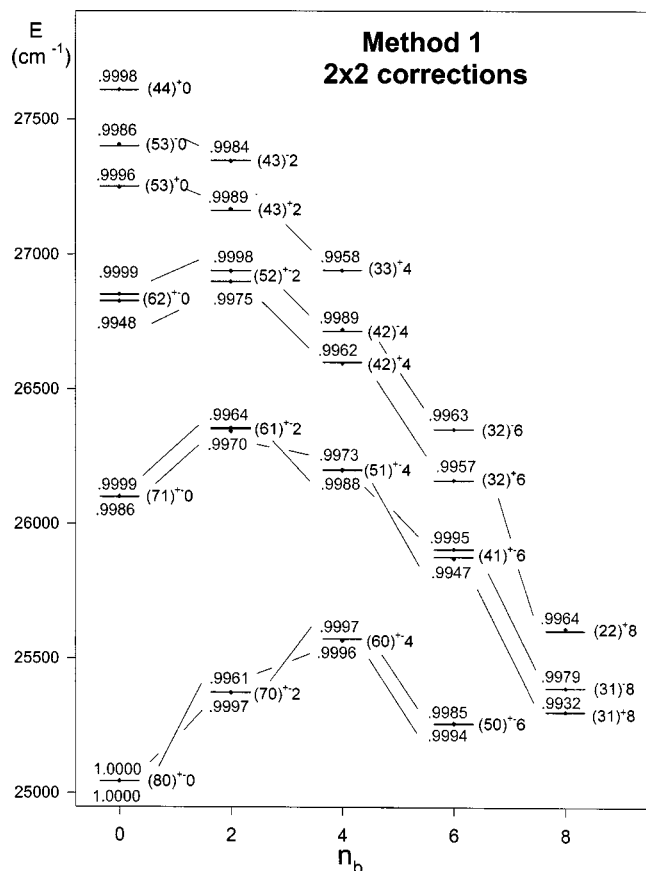


FIG. 3. Results of method 1 corrected with 2×2 matrices, as described in Sec. V A. The pairs of levels corrected in 2×2 matrices are indicated in Table I. See Fig. 2 caption for explanation of symbols.

vectors of 0.7892 and 0.7882. The other bad cases are $(5,1)^+4$ and $(3,2)^+6$, with overlaps 0.8810 and 0.8782. The main cause of the problem is evident: in each case, the near degeneracy of a pair $|\psi_i\rangle, |\psi_j\rangle$. In the 2×2 basis of exact states $|\psi_i\rangle, |\psi_j\rangle$, any difference between H^{full} and H^{eff} will lead to mixing of the exact states by off-diagonal matrix elements $\langle \psi_i | H^{full} - H^{eff} | \psi_j \rangle$. If the exact pair were truly degenerate, any mixing, no matter how small, would lead to overlaps with the H^{eff} eigenstates of $1/\sqrt{2}$; this nearly happens with $(6,1)^-2$ and $(3,2)^-6$.

This can be turned around to say that 2×2 mixing $\langle \psi_i^{eff} | H^{full} - H^{eff} | \psi_j^{eff} \rangle$ of the near-degenerate pair of eigenstates of H^{eff} should give states very close to the pair of exact eigenstates $|\psi_i\rangle, |\psi_j\rangle$ of H^{full} . We tested this in the present case by diagonalizing 2×2 matrices constructed in the basis of eigenstates ψ_i^{eff} of H^{eff} , with diagonal and off-diagonal elements computed for $\langle \psi_i^{eff} | H^{full} - H^{eff} | \psi_j^{eff} \rangle$. The overlaps for the two exceptional pairs improve dramatically, as shown in Fig. 3 and Table I, to 0.9964, 0.9963 and 0.9973, 0.9957. We experimented with improving three other pairs of levels in this way, obtaining enhanced results in each case, as shown in Fig. 3 and Table I. We also experimented with applying this procedure to 3×3 and larger matrices. As expected, the results with these larger matrices were not dramatically better, and are not shown.

There is a close connection of this situation with “dynamical tunneling”^{39,40} between a pair of accidentally near-

degenerate approximate states, which unavoidably leads to a strong mixing of the approximate states, no matter how good the approximate Hamiltonian. Indeed, it has been noted by Keshavamurthy and Ezra^{23,24} that the mixing of the states under consideration is due primarily to dynamical tunneling, rather than effects of classical chaos.

3. Intensities in the dressed basis

Method 1 has worked remarkably well for the energies and overlaps, which are 0.993 or greater for all states after correction for unavoidable near degeneracies. An important question is how well the eigenstates of the effective Hamiltonian can reproduce observable properties of eigenstates of the full Hamiltonian, other than the energies. An obvious example is intensities. To test this, we modeled the intensities of absorption spectra, supposing that the entire transition moment is contained in the pure zero-order stretch overtones $|8,0,0\rangle, |0,8,0\rangle$. This results in the intensities shown in Fig. 4(a). (Note the \log_{10} scale, for a vast range of intensities.) For method 1 without 2×2 corrections, the intensities given by the pure overtone model are shown in Fig. 4(b). For the most part, the intensities agree well with those of H^{full} . However, there are some notable exceptions. In particular, in the two “bad” pairs discussed above, the intensity of one of each pair is seriously underestimated. When the 2×2 corrections are applied, the resulting intensities, shown in Fig. 4(c), are greatly improved. The remaining anomalies are for a few extremely weak transitions.

The foregoing has demonstrated (1) that the effective Hamiltonian of method 1 reproduces the eigenenergies of the full Hamiltonian very well, (2) the eigenvectors have excellent overlap with the eigenvectors of the full Hamiltonian in most cases, (3) in the exceptional cases of near degeneracy, the overlaps are dramatically improved with the use of 2×2 matrices, related to dynamical tunneling; and (4) most intensities are reproduced extremely well by the effective Hamiltonian.

For comprehensiveness, we summarize results for all the polyads $P = 1 - 8$ in Table II. For each polyad, we report the root-mean-square overlap of the eigenvectors of the dressed basis Hamiltonian with those of the spectroscopic Hamiltonian. The results are completely consistent with those presented in detail for polyad 8. Not surprisingly, the rms overlap is better for lower polyads, where the symmetric stretch and bend are less well tuned to 2:1 resonance.

B. Method 2: Dressed local stretch–bend modes with effective stretch–stretch resonance

The second Hamiltonian, by analogy to the naive independent-resonance approximation (10), has a dressed zero-order basis with bends and local stretches coupled by the stretch–bend Fermi interaction and an effective residual stretch–stretch coupling:

$$H_{SS}^{L, dr} = H_{OSS}^{L, dr} + V_{SS}^{L, eff}. \quad (18)$$

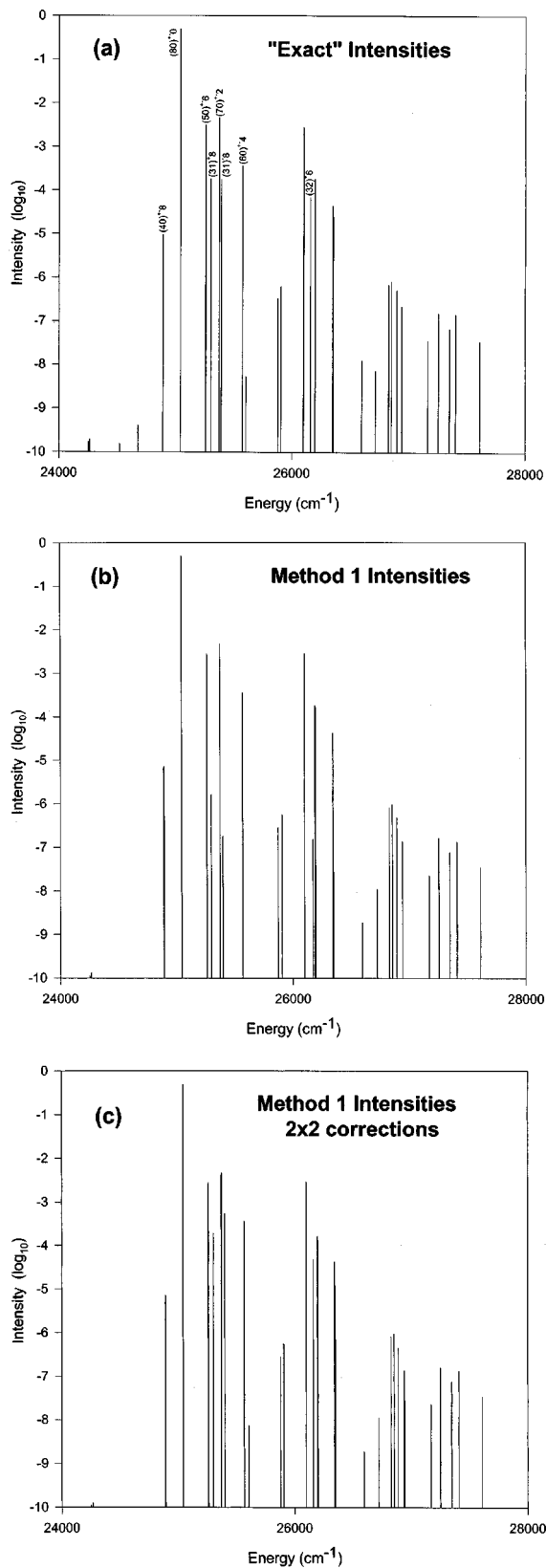


FIG. 4. Comparison of intensities for exact and effective Hamiltonians. Section V A 3 describes model for calculating intensities. (a) Intensities of the exact Hamiltonian, (b) intensities calculated in method 1, (c) intensities calculated in method 1 with 2×2 corrections. Some key levels are identified by their assignments, which may be compared with Figs. 2 and 3 and Table I.

TABLE II. Root-mean-square overlap of eigenvectors of the dressed basis Hamiltonian with those of the spectroscopic Hamiltonian for polyads $P = 1 - 8$.

Polyad No.	rms overlap
1	1.0000
2	0.9999
3	0.9996
4	0.9994
5	0.9964
6	0.9944
7	0.9911
8	0.9824

We follow the same three steps as in method 1. Following the general definition (13), we define $H_{0SS}^{L, dr}$ as the original zero-order H_0^L dressed by V_F^L , the stretch-bend coupling in the local basis:

$$H_{0SS}^{L, dr} = H_0^L + V_F^L \quad (19)$$

The next step is to assign nominal zero-order local-mode quantum numbers to this dressed basis. Since the dressed zero-order Hamiltonian contains the stretch-bend coupling V_F^L , though its eigenstates have good total stretch-bend polyad quantum number $(n_1 + n_2 + n_b/2)$, they are strong mixtures of the original zero-order stretch-bend basis states. From our earlier single-resonance analysis,^{3,5,6} we know that they do not all have stretch and bend mode character. Within a sequence with fixed $(n_1 + n_2 + n_b/2)$, some of the states have undergone a transition to a type of motion called “resonant modes.” As in method 1, we nonetheless want to assign a single set of nominal quantum numbers $(n_1, n_2, n_b)^{nom}$ to the dressed zero-order basis. For example, consider the sequence with $(n_1 + n_2 + n_b/2) = 8$. The states of the dressed basis are assigned as $(8, 0, 0)^{\pm nom}$, $(7, 0, 2)^{\pm nom}, \dots, (0, 0, 16)^{\pm nom}$. As in method 1, we do this following a correlation diagram procedure, this time exactly the one used in Ref. 13. The coupling V_F^L is turned on and the labels $(n_1, n_2, n_b)^{\pm}$ carried diabatically from the zero-order basis for H_0^L to the dressed basis. (This is the procedure of nominal assignments followed in Fig. 8 of Ref. 13 going from the left to the center of the diagram.)

The final step is to define matrix elements of $V_{SS}^{L, eff}$ in terms of the nominal quantum number assignments. By analogy with Eqs. (4), (5), and (7), we take $V_{SS}^{L, eff}$ to be of the form

$$V_{SS}^{L, eff} = V_{1:1}^{L, eff} + V_{2:2}^{L, eff}, \quad (20)$$

where

$$V_{1:1}^{L, eff} = \left[\lambda + \lambda'(n_1 + n_2 + 1) + \lambda'' \left(n_b + \frac{1}{2} \right) \right]^{nom} \times (a_1 a_2^\dagger + a_2 a_1^\dagger) \quad (21)$$

and

$$V_{2:2}^{L, eff} = \gamma (a_1 a_1 a_2^\dagger a_2^\dagger + a_2 a_2 a_1^\dagger a_1^\dagger), \quad (22)$$

with the parameters $\lambda, \lambda', \lambda'', \gamma$ taken from the fit of Baggott,³³ analogous to method 1.

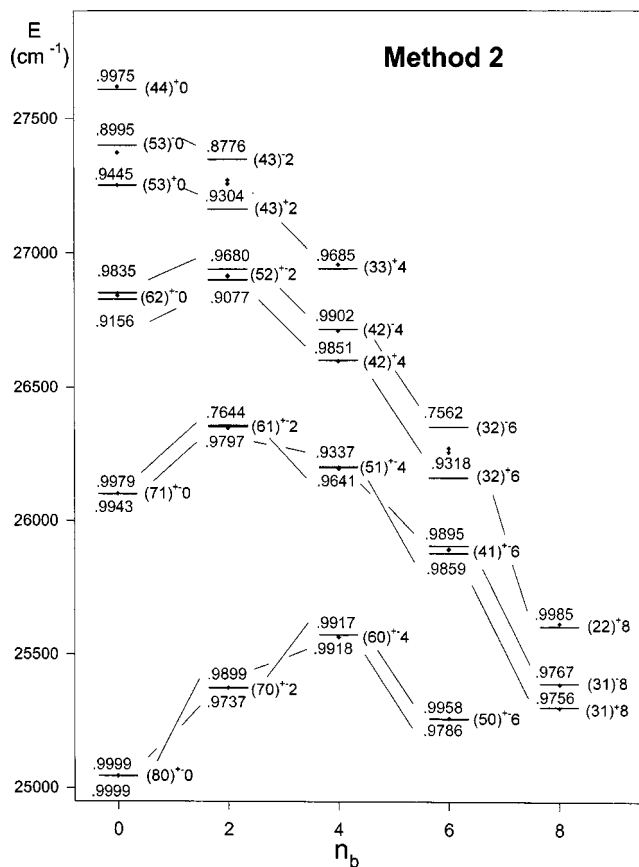


FIG. 5. Results for energies and eigenvectors using method 2 with effective Hamiltonian $H_{SS}^{L,dr}$, described in Sec. V B. See Fig. 2 caption for further explanation of symbols.

Figure 5 and Table I show the results of method 2. The spectrum and eigenvectors of $H_F^{L,dr}$ are compared with those of H^{full} . The agreement of the exact and effective energies, as well as the eigenvector overlaps, is again excellent in most cases, though not as good as with method 1. There are some cases in Fig. 5 of serious discrepancies in the energies, in particular $(4,3)^{\pm 2}$ and $(3,2)^{\pm 6}$. Correction of problematic cases with 2×2 matrices again leads to improved results, though not quite as good as in method 1. The reason for the errors in the energies before the 2×2 corrections is that H^{full} and H^{eff} differ slightly for these states, so non-negligible diagonal matrix elements of $\langle \psi_i^{eff} | H^{full} - H^{eff} | \psi_i^{eff} \rangle$ arise in the correction procedure. The results with 2×2 corrections are given in Table I, but not shown pictorially.

C. Choice of method

The numerical tests have shown that the dressed basis approach gives a surprisingly good approximation to the exact Hamiltonian in both methods. What lessons can we draw from this?

Method 1 works best for the eigenstates because it constructs the zero-order basis by dressing with the *strong* stretch–stretch coupling. The weaker Fermi resonance is then accounted for approximately as a residual effective Fermi coupling. The lesson is that in constructing the zero-order dressed basis, it works best to include the strongest

resonance (or resonances, by extension to molecules with many couplings). However, the still impressive success of method 2 shows that if desired, one can also choose to dress with the weak coupling and retain the strong coupling as the residual effective resonance. This flexibility in choosing the residual coupling can be important depending on the kinds of questions one is asking about the system.

VI. WHAT DO THE NOMINAL EFFECTIVE QUANTUM NUMBERS MEAN?

As emphasized in Sec. II, the nominal effective quantum numbers are not rigorous constants. A key issue then is, what is their status in light of the numerical results on the dressed basis sets? First, it is necessary to reiterate a crucial distinction between two different uses of the term “nominal assignment” in this paper. First, there are the nominal quantum numbers of the dressed *zero-order* basis. Second, as in Table I and Figs. 2–5 and earlier in Refs. 11, 13, and 36–38, we made nominal assignments of the *eigenstates* of the full spectroscopic Hamiltonian. We will assess the utility of the nominal assignments in both senses.

A. Assigning the dressed zero-order basis

The *zero-order* nominal assignments for each dressed basis slice the polyad in various ways into subpolyads in which an effective resonance acts. The surprisingly good numerical results demonstrate the utility of the nominal zero-order assignments. This supports the conceptual hypothesis behind the nominal assignments, presented in Sec. V A, that the character of the zero-order basis states of H_0 does not change too much in the diabatic correlation to H_0^{dr} .

B. Classifying the eigenstates

Now we turn to the related procedure of making nominal assignments of *eigenstates*, used here and earlier in Refs. 11, 13, and 36–38. These are a complete set of N quantum labels and therefore useful for identifying analogs of sequences and progressions in the eigenstate spectrum. Here, they are obtained by continuing the nominal assignments of the zero-order dressed basis along the diabatic curves of the correlation diagram as the remainder of the full Hamiltonian is turned on.

With the assignment of nominal quantum numbers, we can slice the spectrum of eigenstates in various ways into sequences with a fixed value of one of the N nominal quantum numbers. For example, one type of sequence division, into stretch–stretch subpolyads, is given by the columns with fixed nominal bend quantum number n_b in Figs. 2, 3, and 5. Another type of division, into stretch–bend Fermi sequences, is given by the “arches” of levels connected in the figures by straight line segments. The spectral pattern within columns exhibits the division between local and normal character of the stretches; the arches exhibit the influence of the stretch–bend Fermi resonance known from earlier single-resonance analysis.¹⁰

These spectral patterns are an indication that the nominal eigenstate assignments in Refs. 11, 13, and 36–38 are identifying slicings or sequences of the spectrum in which the eigenstates are approximately characterized by an independent effective resonance. The calculations here give numerical evidence that further supports this idea.

VII. SUMMARY AND CONCLUSIONS

This paper has shown how to construct dressed or pre-diagonalized bases, in each of which a multiresonance Hamiltonian is successfully approximated by a single effective resonance. This largely incorporates the effects of non-integrability, while furnishing much of the simplicity of integrable, single-resonance systems. This mirrors the observed decomposability^{11,12} of the bifurcation structure of the multiresonance spectroscopic Hamiltonian into a sequence of simple single-resonance bifurcations. Numerically, the success of the method far exceeds expectations.

It would be very useful if one could use various choices of dressed zero-order basis and residual V_i^{eff} to give effective Hamiltonians amenable to simplified single-resonance bifurcation analysis. By combining the perspectives of several dressed bases, each with its own effective resonance, it would be possible to simplify interpretation of the standard multiresonance spectroscopic Hamiltonian, where bifurcation analysis is feasible,^{12,15} but rapidly becomes very complicated with increasing system size. We are now testing this on C_2H_2 spectra and investigating the dynamical knowledge that can be obtained.

The ability to slice the system in different ways, each associated with its own dressed basis and subpolyads in which there acts an effective residual resonance coupling, suggests that it may be useful to think of energy transfer pathways or “channels.” The effective coupling is confined within a channel by its effective single-resonance structure, for time scales less than the time scale for which the dressed basis approximation is valid. This may find use for analyzing intramolecular energy transfer processes.

The dressed basis approach as developed so far has assumed the existence of a polyad number, corresponding to an approximate constant of motion valid for short time scales of intramolecular energy flow. The true molecular Hamiltonian undoubtedly contains terms which break the polyad number at longer time scales, corresponding to finer levels of detail in the spectrum. Associated with their inclusion is a large increase in basis size, because the block diagonalization of the polyad number is lost. However, the basic polyad spectral pattern may not be greatly altered.⁴¹ This suggests an approach in which the entire polyad Hamiltonian is used to

construct the dressed zero-order basis, with a given polyad-breaking resonance treated as an effective residual operator.

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