

Nonadiabatic corrections for coupled Morse oscillators using Hutson and Howard perturbation theory

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An adiabatic separation is applied to two coupled Morse oscillators. The resulting approximate energies and wavefunctions are corrected for nonadiabatic interactions by means of the perturbation theory approach of Hutson and Howard supplemented by the “Padé divergent series summation” technique. The convergence properties of the perturbation series are investigated as functions of the oscillator frequencies and coupling strengths varying over a wide range of values. The rate of convergence and accuracy of summability of the perturbation series depend strongly on the presence of accidental resonances among the adiabatic levels. For relatively well isolated levels, the series either converge strongly or can be summed very accurately for almost any strength of perturbation. In the case of close coincidence of more than two strongly coupled levels, the approach becomes unreliable. The convergence/summability problems faced in the “intermediate” cases of two “adiabatically crossing” levels appear to be curable by means of interpolating over the “near-degeneracy” regions. © 1995 American Institute of Physics.

I. INTRODUCTION

The development of accurate and efficient methods for calculating bound- and metastable-state energy levels of polyatomic molecules is a topic of considerable current interest. This is driven partly by the progress in experimental techniques which allow for direct spectroscopic probing of molecular states over a wide range of excitations (see, e.g., Ref. 1) and partly by the urgent needs to rationalize the vibrational energy transfers induced by the selected state-to-state excitations (see, e.g., Ref. 2).

For low dimensional problems there are many techniques available which have recently been used with considerable success (an excellent review can be found in Refs. 3–4). In the case of high dimensional problems, however, all these techniques become plagued by serious drawbacks. Traditionally the most widely used perturbative approaches are hampered by the fact that the perturbation series expansions may not converge even for relatively small anharmonic perturbations.⁵ Numerically robust and “easily” implementable basis-set methods, despite very impressive achievements either in designing very efficient basis-set contraction schemes^{6,7} or in constructing suitably sparse Hamiltonian matrices,^{8,9} seem to be bound to systems consisting of less than five atoms if all degrees of freedom are to be respected. Very flexible “basis-set-independent” finite-difference and finite-element methods,¹⁰ which are of no competition in the case of the one-dimensional problems, are already impractical in the case of three dimensions. A similar conclusion can also be given in the case of the collocation methods which have recently become popular due to their simplicity.¹¹

Apparently, a complete theoretical description of the dynamics of a molecular system consisting of more than four atoms is a rather unfeasible task. On the other hand, since the couplings between the vibrational modes of bigger systems are unlikely to be of the same strength, the high dimensional problems pertaining to these systems may become approximately separable into smaller ones according to the strength of the couplings (see, e.g., Ref. 12). Internal dynamics of the subsystems can be treated separately by the stable and accurate (but “expensive”) variational procedures, and the weak “intersystem” couplings accounted for by means of “cheap” methods of perturbation theory. One of the most natural ways for performing such a separation is based on the adiabatic (Born–Oppenheimer) approximation (see, e.g., Ref. 13). To get a detailed insight on the prospects of this approach, recently, we have performed model calculations for a pair of harmonic oscillators anharmonically coupled by the cubic and quartic terms. The actual calculations were performed using the Rayleigh–Schrödinger perturbation theory approach of Hutson and Howard,¹⁴ in which we start from the adiabatic approximation and treat the nonadiabatic corrections as perturbations. Though the corresponding perturbation series were found to be rather prone to diverge, for the adiabatic levels away from “accidental resonances” they have been found accurately summable by means of the Padé approximant summation technique^{15,16} even in the cases of very strong couplings. In this study we generalize our “divergent series” approach to the case of two coupled Morse oscillators. The Morse oscillators are ideal model systems for describing stretching vibrational motions. Thus an accurate description of their dynamics by means of perturbation theory may be of some very practical consequences for description of real molecular systems.

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II. THEORY

The Hutson and Howard perturbation theory has already been described in detail in the literature,^{14,17} therefore, we provide here only a brief outline of its use in the present problem. We consider a pair of coupled Morse oscillators which is described by the following Hamiltonian:

$$\mathbf{H} = -\frac{\partial^2}{\partial x^2} + V_x[1 - \exp\{-\omega_x x\}]^2 - \frac{\partial^2}{\partial y^2} + V_y[1 - \exp\{-\omega_y y\}]^2 + V_{xy}[1 - \exp\{-\omega_x x\}] \times [1 - \exp\{-\omega_y y\}], \quad (1)$$

where V_x , V_y , V_{xy} , ω_x , and ω_y are given constants.

Now, exactly in the same manner as in Ref. 17, the x coordinate is taken as the “high-frequency” motion coordinate and, within the framework of the Born–Oppenheimer approximation, the wave functions describing this motion will be written as $X(x;y)$ and the corresponding eigenvalues as $U(y)$. These eigencharacteristics are solutions of the Schrödinger equations for the Hamiltonians obtained from Eq. (1) by fixing values of y and neglecting derivatives with respect to y . The adiabatic energy levels, E_{nj} , and corresponding wave functions, $Y_{nj}(y)$, are obtained as solutions of the following Schrödinger equations:

$$\left\{ -\frac{d^2}{dy^2} + U_j(y) + \tau_{jj}^{(2)} - E_{nj} \right\} Y_{nj}(y) = 0, \quad (2)$$

where $\tau_{jj}^{(2)}$ are diagonal matrix elements of the nonadiabatic perturbation terms and

$$U_j(y) = (2j+1)\omega_x\sqrt{V_x} + V_y[1 - \exp\{-\omega_y y\}]^2 - \omega_x^2(V_{xy}[1 - \exp\{-\omega_y y\}]/2\omega_x\sqrt{V_x} - (j+1/2))^2. \quad (3)$$

The nonadiabatic perturbation, \mathbf{H}' , is best defined by the matrix elements in the adiabatic basis, i.e.,

$$\langle X_i(x;y) | \mathbf{H}' | X_j(x;y) \rangle = H'_{ij} = 2\tau_{ij}^{(1)} \frac{d}{dy} + \tau_{ij}^{(2)}(1 - \delta_{ij}), \quad (4)$$

where

$$\tau_{ij}^{(1)} = \langle X_i(x;y) | -\frac{\partial}{\partial y} | X_j(x;y) \rangle_x, \quad (5)$$

$$\tau_{ij}^{(2)} = \langle X_i(x;y) | -\frac{\partial^2}{\partial y^2} | X_j(x;y) \rangle_x. \quad (6)$$

($\langle \rangle_x$ means integration over the x coordinate only.)

III. RESULTS AND DISCUSSION

To get insight on the prospects of this approach in the case of typical molecular systems, the actual calculations have been carried out for oscillators imitating (not too closely) the stretching potentials of the O–H fragments of water (namely, we used $\omega_x = \omega_y = 2.2241$; for details see Refs. 18 and 19). To probe the effectiveness of the adiabatic separation of the “fast” and “slow” motions, four formal “isotopes” of water were respected here by choosing the following “diagonal” force constants [in units providing the corresponding Hamiltonian in its “canonical” form (1)]:

$$\text{Case A: } V_x = 2400, \quad V_y = 600,$$

$$\text{Case B: } V_x = 2400, \quad V_y = 1200,$$

$$\text{Case C: } V_x = 2400, \quad V_y = 2000,$$

$$\text{Case D: } V_x = 2400, \quad V_y = 2400.$$

To probe the behavior of the perturbation theory, the perturbation series were investigated as functions of the coupling constant V_{xy} varying over a wide range of values (*vide infra*).

The adiabatic energies, E_{nj} , and wave functions, Y_{nj} , were calculated using the standard Numerov–Cooley method²⁰ on a grid of 2000 points for $y \in [-0.5, 4.9]$. The nonadiabatic matrix elements, $\tau_{ij}^{(1)}$ and $\tau_{ij}^{(2)}$, were obtained using the formulae given by Child.²¹ The perturbation series were processed using the symbolic language Maple (Ref. 22), which allowed for preserving adequate accuracy even in the case of strong divergence. To allow for comparisons, the energies and wave functions of the studied models have also

TABLE I. Convergence properties^a of the standard RSPT for Case A.

State [j, n]	E_0^b	$V_{xy} = -1800$	$V_{xy} = -1200$	$V_{xy} = -600$	$V_{xy} = -150$	$V_{xy} = 150$	$V_{xy} = 600$	$V_{xy} = 1200$
[0,0]	160.96	N_{14}	N_9	N_5	N_3	N_3	N_6	N_{18}
[0,1]	260.03	N_{17}	N_{11}	N_6	N_3	N_3	N_7	N_{26}
[0,2]	349.20	N_{20}	N_{12}	N_{11}	N_4	N_5	N_{15}	N_{27}
[1,0]	368.99	$P_6(5)$	$P_8(9)$	N_9	N_5	N_5	N_{12}	$P_8(6)$
[0,3]	428.48	N_{22}	N_{18}	N_7	N_3	N_4	N_8	N_{24}
[1,1]	468.05	$P_5(5)$	N_{12}	N_{14}	N_5	N_5	N_{25}	N_{27}
[0,4]	497.86	N_{23}	$P_{10}(8)$	N_8	N_3	N_4	N_{17}	$P_{11}(5)$
[1,2]	557.22	$P_6(5)$	$P_8(6)$	N_{17}	D	$P_9(6)$	$P_{12}(6)$	D
[0,5]	557.36	N_{24}	N_{19}	$P_8(9)$	D	$P_{11}(6)$	$P_{10}(7)$	$P_8(9)$
[2,0]	567.12	$P_4(5)$	D	N_{14}	N_7	N_9	$P_{10}(9)$	$P_{12}(5)$

^a N_m : the RSPT series converges and provides the corresponding eigenvalue accurate at least to one part in 10^9 in the m th order; $P_m(n)$: the RSPT series diverges (or fails to converge in 27 perturbation steps) and can be summed approximately with accuracy one part in 10^n by means of the Padé approximant of the m th order; D : the RSPT series diverges and is summable with lower accuracy than one part in 10^5 .

^bEnergy of the uncoupled oscillators (i.e., $V_{xy} = 0$).

TABLE II. Case A; $V_{xy} = -150$. Energy perturbation series for the [1,2] state.

Order of PT	$V_y=595$	$V_y=600$	$V_y=605$
2	0.995		-67.988
3	-0.003		0.094
4	-0.975		180 854.172
5	0.004		-508.794
6	1.660		-964 318 546.368
7	-0.010		4 069 342.399
8	-3.535		6 427 214 767 624.132
9	0.028		-36 163 054 805.055
10	8.434		-47 978 113 687 339 352.000
11	-0.082		337 439 107 685 242.690
12	-21.559		38 373 089 208 826 390 000.000
13	0.252		-323 862 167 285 958 140.000
14	57.735		-321 524 261 728 260 300 000 000.000
15	-0.786		3 165 876 513 324 865 400 000.000
16	-159.890		2 785 861 102 536 636 000 000 000 000.000
17	2.488		-31 349 571 720 623 890 000 000 000.000
18	454.154		-24 757 144 738 849 539 000 000 000 000.000
19	-7.949		313 418 926 932 777 740 000 000 000 000.000
20	-1315.792		224 409 803 181 657 690 000 000 000 000 000.000
21	25.587		-315 663 211 429 075 070 000 000 000 000 000.000
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	$E(0)^a=553.301$	$E(0)=554.451$	$E(0)=555.596$
	[11/11]=553.888	[10/10]=554.438	[12/12]=554.577
	[11/12]=553.888	[10/11]=548.764	[12/13]=554.577
		Interp ^b =552.914	
		Var ^c =552.964	

^aAdiabatic energy.^bInterpolated value.^cVariational calculation.TABLE III. Case A; $V_{xy} = 150$. Energy perturbation series for the [0,5] state.

Order of PT	$V_y=595$	$V_y=600$	$V_y=605$
2	-1.563		9.555
3	0.002		-0.014
4	1.452		-538.729
5	-0.005		1.432
6	-3.213		59 144.334
7	0.017		-235.814
8	8.891		-8 116 434.580
9	-0.062		43 146.689
10	-27.554		1 247 485 978.703
11	0.238		-8 289 379.030
12	91.489		-205 432 590 878.135
13	-0.948		1 638 074 529.690
14	-318.241		35 441 037 597 886.945
15	3.848		-329 697 357 300.121
16	1144.719		-6 322 695 205 416 504.000
17	-15.814		67 220 510 781 447.359
18	-4223.130		115 689 369 965 286 730.000
19	65.625		-13 837 081 638 378 278.000
20	15891.639		-21 591 600 707 514 420 000.000
21	-274.354		286 940 989 931 837 030.000
22	-60759.436		4 094 380 686 587 198 600 000.000
23	1153.752		-59 853 292 223 358 553 000.000
24	235361.256		-786 626 788 715 836 720 000 000.000
25	-4875.208		12 544 594 497 005 477 000 000.000
26	-921726.081		152 790 263 036 914 130 000 000 000.000
27	20682.295		-2 639 643 534 528 307 200 000 000.000
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	$E(0)^a=551.989$	$E(0)=554.503$	$E(0)=557.007$
	[12/12]=550.950	[11/11]=554.949	[12/12]=557.567
	[12/13]=550.950	[11/12]=556.853	[12/13]=557.567
		Interp ^b =555.578	
		Var ^c =555.582	

^aAdiabatic energy.^bInterpolated value.^cVariational calculation.

TABLE IV. Convergence properties^a of the standard RSPT for Case B.

State $[j, n]$	E_0^b	$V_{xy} = -1200$	$V_{xy} = -600$	$V_{xy} = -150$	$V_{xy} = 150$	$V_{xy} = 600$	$V_{xy} = 1200$
[0,0]	183.53	N_{10}	N_5	N_3	N_3	N_6	N_{12}
[0,1]	327.72	N_{19}	N_9	N_3	N_3	N_9	N_{20}
[1,0]	391.55	N_{13}	N_9	N_3	N_4	N_8	N_{19}
[0,2]	462.03	N_{15}	N_7	N_3	N_3	N_8	N_{22}
[1,1]	535.75	$P_{11}(8)$	N_{19}	N_5	N_5	N_{26}	$P_{11}(5)$
[0,3]	586.44	$P_8(7)$	$P_8(9)$	N_8	N_9	$P_7(8)$	$P_8(8)$
[2,0]	589.68	N_{26}	N_{20}	N_7	N_8	N_{19}	N_{26}
[1,2]	670.05	$P_{11}(5)$	$P_{10}(9)$	N_7	N_7	$P_{10}(8)$	D
[0,4]	700.96	$P_9(6)$	N_{26}	N_7	N_9	$P_9(8)$	D
[2,1]	733.88	$P_8(6)$	$P_9(9)$	N_7	N_7	$P_{11}(9)$	D
[3,0]	777.92	$P_8(7)$	$P_{11}(6)$	N_7	N_7	$P_{11}(5)$	$P_{10}(5)$
[1,3]	794.46	D	D	N_{15}	N_{21}	D	D
[0,5]	805.58	D	$P_{10}(6)$	N_{15}	N_{19}	D	D
[2,2]	868.18	D	$P_{10}(9)$	N_7	N_8	$P_{11}(5)$	D
[0,6]	900.31	D	D	N_{26}	N_{19}	$P_8(6)$	D
[1,4]	908.98	$P_{10}(5)$	D	N_{26}	N_{17}	D	D
[3,1]	922.11	D	$P_{11}(8)$	N_9	N_9	D	D
[4,0]	956.26	$P_{10}(5)$	D	N_7	N_9	D	$P_9(5)$
[0,7]	975.15	D	D	N_{11}	N_9	$P_{10}(6)$	D
[2,3]	992.59	D	D	N_{15}	N_{15}	$P_9(5)$	D
[1,5]	1013.60	D	$P_{10}(6)$	N_{13}	N_{15}	$P_{11}(6)$	D
[3,2]	1056.42	D	$P_{11}(5)$	N_9	$P_8(9)$	$P_{10}(6)$	D
[0,8]	1060.09	D	$P_{10}(7)$	N_9	$P_4(9)$	D	D
[4,1]	1100.46	D	D	$P_{11}(9)$	N_{17}	D	D
[2,4]	1107.11	$P_{11}(5)$	D	D	D	$P_{10}(5)$	D
[1,6]	1108.33	D	D	D	D	$P_7(5)$	D
[5,0]	1124.71	D	$P_6(5)$	N_{11}	$P_7(9)$	$P_{10}(6)$	D
[0,9]	1125.14	D	$P_6(6)$	N_{13}	$P_7(9)$	D	D
[0,10]	1180.30	D	D	$P_6(9)$	N_{13}	$P_9(7)$	D
[3,3]	1180.83	D	D	$P_{10}(8)$	N_{15}	D	D
[1,7]	1193.17	D	$P_9(5)$	N_{17}	N_{15}	D	D

^a N_m : the RSPT series converges and provides the corresponding eigenvalue accurate at least to one part in 10^9 in the m th order; $P_m(n)$: the RSPT series diverges (or fails to converge in 27 perturbation steps) and can be summed approximately with accuracy one part in 10^n by means of the Padé approximant of the m th order; D : the RSPT series diverges and is summable with lower accuracy than one part in 10^5 .

^bEnergy of the uncoupled oscillators (i.e., $V_{xy}=0$).

been evaluated variationally. The corresponding basis sets were constructed as products of the eigenfunctions of the uncoupled Morse oscillators. The number of the basis set functions were chosen so that the energies of the required states were converged to an accuracy of 1 to 10^5 .

The results characterizing our calculations are collected in Tables I–VI. In Table I we present convergency characteristics of all the bound states of our model systems of Case A (strictly speaking, the bound states of the most weakly coupled systems). We see in the table that for the majority of states the Hutson and Howard perturbation series are either strongly converging or summable, highly accurately, by means of Padé approximants. The failure in convergence, which is faced in only a few cases, is caused by the accidental resonances of the actual adiabatic levels. Quite generally, the “resonances” manifest themselves mathematically as singularities in the differential equations for the perturbation corrections. Due to these singularities, the perturbative approach collapses entirely at the “exact degeneracy,” and leads to rather wild divergence in the regions of “near degeneracy” (for more details see Ref. 17). Outside these regions, however, the perturbation series behave properly. Typical examples of such behavior in our case are provided by the series corresponding to the closely coinciding [1,2]

and [0,5] energy levels of the discussed model. We see in Tables II and III that the adiabatic energies of these levels evaluated at $V_y=600$ are practically coinciding. Accordingly, the corresponding perturbation series diverge too strongly even for the Padé summation technique (as a convenient criterium of convergency we can use degree of coincidence in the $[i/i]$ and $[i/i+1]$ Padé approximants²³ which usually bracket the true value of the sought sum). On the other hand, however, the perturbation series corresponding to only slightly “detuned” levels (detuned by changing the values of V_{xy} from 600 to 595 and 605, respectively) can be summed with a high accuracy. We find it worth noting that the series corresponding to the [1,2] and [0,5] levels were found to be summable with accuracy 1 part in 10^6 even for $V_{xy}=597.5$ and 602.5, respectively! The possibility of accurate summation of the perturbation series very close to the regions of degeneracy allows, obviously, for a reasonable determination of the degenerate energies by interpolating over these regions. In Tables II and III we can see that a simple polynomial interpolation (based on knowledge of accurate energies corresponding to $V_{xy}=580, 590, 595, 605, 610,$ and 620) provides the “ $V_{xy}=600$ ” energies with a fairly acceptable accuracy.

In Tables IV–VI we summarize information on the con-

TABLE V. Convergence properties^a of the standard RSPT for Case C.

State $[j, n]$	E_0^b	$V_{xy} = -1200$	$V_{xy} = -600$	$V_{xy} = -150$	$V_{xy} = 150$	$V_{xy} = 600$	$V_{xy} = 1200$
[0,0]	205.95	N_{10}	N_6	N_3	N_3	N_6	N_{11}
[0,1]	394.98	$P_9(5)$	$P_{10}(8)$	N_9	N_9	$P_{10}(9)$	$P_9(5)$
[1,0]	413.97	$P_{10}(7)$	$P_9(9)$	N_9	N_9	$P_7(7)$	$P_{10}(7)$
[0,2]	574.13	$P_9(5)$	$P_{11}(9)$	N_7	N_7	$P_{10}(8)$	$P_{10}(5)$
[1,1]	603.01	D	$P_{10}(5)$	$P_9(9)$	$P_8(9)$	D	D
[2,0]	612.10	$P_{10}(5)$	$P_9(6)$	$P_8(9)$	$P_8(9)$	$P_9(5)$	D
[0,3]	743.38	$P_{11}(6)$	N_{25}	N_6	N_6	N_{21}	$P_8(5)$
[1,2]	782.15	D	D	N_{14}	N_{15}	D	D
[3,0]	800.34	D	D	D	D	D	D
[2,1]	801.14	D	D	D	D	D	D
[0,4]	902.73	$P_8(5)$	N_{17}	N_5	N_5	N_{17}	D
[1,3]	951.40	D	D	N_9	N_9	D	D
[4,0]	978.68	D	D	D	D	D	D
[2,2]	980.28	D	D	D	D	D	D
[3,1]	989.37	D	D	$P_9(6)$	$P_{10}(6)$	D	D
[0,5]	1052.20	D	N_{13}	N_5	N_7	N_{26}	D
[1,4]	1110.76	D	$P_{10}(9)$	N_8	N_7	$P_{10}(5)$	D
[5,0]	1147.12	D	D	D	$P_{10}(7)$	D	D
[2,3]	1149.53	D	D	D	$P_{11}(7)$	D	D
[4,1]	1167.72	D	D	D	D	D	D
[3,2]	1168.52	D	D	D	D	D	D
[0,6]	1191.77	D	$P_{10}(9)$	N_9	N_{11}	$P_8(6)$	D
[1,5]	1260.22	D	$P_6(7)$	N_7	N_7	$P_9(6)$	D
[6,0]	1305.69	D	D	$P_8(7)$	N_{20}	D	D
[2,4]	1308.89	D	D	$P_8(8)$	N_{18}	D	D
[0,7]	1321.44	D	D	N_{13}	N_{15}	D	D
[5,1]	1336.17	$P_9(5)$	D	D	D	D	D
[3,3]	1337.77	D	D	D	D	D	D
[4,2]	1346.86	D	D	$P_9(6)$	$P_{11}(7)$	D	D
[1,6]	1399.79	D	$P_{11}(8)$	N_7	N_9	$P_7(6)$	D
[0,8]	1441.23	D	D	N_9	N_7	D	D
[7,0]	1454.35	D	D	$P_6(9)$	N_{12}	D	D
[2,5]	1458.35	D	D	$P_6(9)$	N_{12}	D	D
[6,1]	1494.72	D	D	D	$P_8(5)$	D	D
[3,4]	1497.12	D	D	D	$P_{11}(6)$	D	D

^a N_m : the RSPT series converges and provides the corresponding eigenvalue accurate at least to one part in 10^9 in the m th order; $P_m(n)$: the RSPT series diverges (or fails to converge in 27 perturbation steps) and can be summed approximately with accuracy one part in 10^n by means of the Padé approximant of the m th order; D : the RSPT series diverges and is summable with lower accuracy than one part in 10^5 .

^bEnergy of the uncoupled oscillators (i.e., $V_{xy}=0$).

TABLE VI. Convergence properties^a of the standard RSPT for Case D.

State $[j, n]$	E_0^b	$V_{xy} = -2400$	$V_{xy} = -1800$	$V_{xy} = -1200$	$V_{xy} = -600$	$V_{xy} = -150$	$V_{xy} = 150$
[0,0]	215.44	N_{27}	N_{16}	N_{11}	N_6	N_3	N_3
[1,0]	423.46	$P_{11}(5)$	$P_{11}(5)$	$P_{10}(5)$	D	D	D
[0,1]	423.46	D	D	D	D	D	D
[2,0]	621.59	D	D	$P_{11}(5)$	D	D	D
[0,2]	621.59	D	D	D	D	D	D
[1,1]	631.48	D	D	D	D	$P_{10}(8)$	$P_8(7)$
[3,0]	809.83	D	D	D	D	D	D
[0,3]	809.83	D	D	D	D	D	D
[2,1]	829.61	D	D	D	D	D	D
[1,2]	829.61	D	D	D	D	D	D
[4,0]	988.17	D	D	D	D	$P_8(6)$	D
[0,4]	988.17	D	D	D	D	$P_9(6)$	$P_{10}(9)$
[3,1]	1017.85	D	D	D	D	D	D
[1,3]	1017.85	D	D	D	D	D	D
[2,2]	1027.74	D	D	D	D	$P_9(7)$	$P_{10}(7)$
[5,0]	1156.62	D	D	D	D	$P_5(9)$	$P_7(7)$
[0,5]	1156.62	D	D	D	$P_{11}(5)$	$P_5(9)$	$P_5(9)$
[4,1]	1196.19	D	D	D	D	D	D
[1,4]	1196.19	D	D	D	D	D	D

^a N_m : the RSPT series converges and provides the corresponding eigenvalue accurate at least to one part in 10^9 in the m th order; $P_m(n)$: the RSPT series diverges (or fails to converge in 27 perturbation steps) and can be summed approximately with accuracy one part in 10^n by means of the Padé approximant of the m th order; D : the RSPT series diverges and is summable with lower accuracy than one part in 10^5 .

^bEnergy of the uncoupled oscillators (i.e., $V_{xy}=0$).

vergence properties of the energy perturbation series pertaining to the models for molecular systems exhibiting motions which are of comparable frequencies. For these systems we do not meet the conditions which are necessary for a reliable performance of the standardlike perturbative approaches (like the approach of Epstein²⁴). For the Hutson and Howard approach, however, a good performance might still be expected provided the nonadiabatic coupling terms are small compared to a typical vibrational energy spacings.^{14,17} In fact, this expectation has been nicely fulfilled, especially for the model systems of Case B. We see in Table IV that with exception of the pair of very closely coinciding [2,4] and [1,6] levels, the perturbation series corresponding to all the bound states of the most weakly coupled model systems ($V_{xy} = -150$ and 150) have been found summable to a very high degree of accuracy. For more strongly coupled oscillators, not surprisingly, the numbers of states for which our procedure failed to provide accurate values of the sought energies was significantly higher (especially in the case $V_{xy} = 1200$). But still, for all the lowest states the procedure performed extremely well.

On increasing the value of the force constant V_y , we increase not only the number of bound states of the studied model systems, but also the number of accidental resonances. Consequently, our nondegenerate perturbative approach loses its efficiency and may be expected to work only for weak couplings and low-lying states. This expectation was found to be in agreement with our results obtained for the model systems of the Case C. We see in Table V that for strong couplings our procedure becomes unreliable even for not too excited states. On the other hand, however, for reasonably “isolated” energy levels and moderate couplings, the procedure still appears as a practical tool for highly accurate calculations. This may be true even in the “equal frequency” case, supposing we are interested only in the ground state vibrational energies. This important finding seems to be strongly backed up by the results pertaining to the degenerate systems of Case D. In Table VI we can see that the ground state perturbation series converge for practically arbitrary couplings. For other states, apparently, application of our approach becomes rather academic.

IV. CONCLUSIONS

Similarly, like in the case of ordinary oscillators,¹⁷ supplementation of the Hutson and Howard perturbation theory approach by the Padé summation technique leads to a significant improvement of its capability in the case of the Morse oscillators. The perturbation series corresponding to relatively isolated adiabatic levels of these oscillators are summable, highly accurately, even if strongly diverging. However, as in the case of ordinary oscillators, the convergency/summability properties of the perturbation series are strongly hampered by the presence of the accidental

coincidences of the adiabatic levels. While in the case of two coinciding levels there is a good chance to overcome this problem by means of a simple “bracketing and interpolating” technique, in the case of three and more closely coinciding states the Padé summation technique becomes inadequate. This “failure” of the Padé summation technique is caused not only by a rather wild divergence in the corresponding series, but also due to rather different “irregularities” in their patterns. An accurate summation of such series is still out of the scope of the available summation techniques.¹⁵

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