

Beyond the  $x$ - $K$  relations  
Calculations of 1-1 and 2-2 resonance constants  
with application to HCN and DCN

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Explicit formulae are given for all off-diagonal 1-1 and 2-2 resonance terms in the vibrational hamiltonian following the first contact transformation. Such formulae are needed to test the quantitative accuracy of the generalized  $x$ - $K$  relation recently published by Della Valle. These formulae are used in a test calculation for linear HCN and DCN and are found only modestly to improve the predicted energy levels for the former, but dramatically improve those of the latter.

### 1. Introduction

The past 15 years have seen an intensive investigation into the nature of the highly anharmonic overtone levels of hydrides [1]. One of the most striking results of this study is how the low resolution structure of overtone spectra can be fitted with precision on the order of 1 part in ten thousand with very simple effective hamiltonians that include the important resonance interactions to lowest order only. One particularly well studied example is the transition to 'local mode' behaviour for the most easily observed overtone levels. Several years ago [2] I published a proof that showed that the widely used Child and Lawton local mode hamiltonian [3] is a special case of a traditional normal mode anharmonic hamiltonian with Darling-Dennison resonance [4]. The off-diagonal 2-2 Darling-Dennison resonance terms are responsible for the recoupling of the problem from normal to local modes. Mills and Robiette published a much more thorough discussion of this point including a derivation of Darling-Dennison interaction terms for molecules of the symmetry of ammonia and methane [5]. If one adopts the Child and Lawton model, which included only the diagonal anharmonicity in the individual bonds, then one arrives at what Mills and Robiette have named ' $x$ - $K$ ' relations which relate all the  $x_{ijs}$  and the off diagonal Darling-Dennison interaction constants ( $K_{ijlms}$ ) in terms of a single bond anharmonic constant,  $x_m$ . These  $x$ - $K$  relations have now been derived for all the common symmetries of equivalent atoms [6, 7].

In a recent paper, Della Valle [8] has extended the algebraic method that I developed [6] for deriving  $x$ - $K$  relations in a way that allows treatment of the coupling of all classes of equivalent atoms. One can easily extend this work to treat the coupling between nonequivalent bond modes. The ' $x$ - $K$ ' relationships will change but the form of the coupling terms will be unchanged. Because of the

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reduced symmetry, these generalized Darling-Dennison interactions couple many more types of states. The effective hamiltonian is once again exactly equivalent to a Child and Lawton type harmonically coupled, anharmonic oscillator hamiltonian which has been widely used in the analysis of overtone spectra [1, 9]. But expressing the hamiltonian in a normal mode basis allows one to more easily incorporate interactions between other degrees of vibrational freedom, and to include vibration-rotation interactions. It is therefore likely that Della Valle's formula will find wide applicability.

In our own work on ammonia [10], we have found that the  $x$ - $K$  relations are not quantitatively accurate. For example, they are in error by as much as  $15 \text{ cm}^{-1}$  for the  $x_{13}$  anharmonic constant. Thus, it is not enough to stop at the ' $x$ - $K$ ' relations, especially if one wants the fitted  $x_m$  constant to be as close as possible to its expected relationship to the single bond stretching potential. What are needed are the full anharmonic expressions for the diagonal anharmonic constants and the off diagonal resonance interaction terms so that the quantitative accuracy of the  $x$ - $K$  relations can be evaluated with a model anharmonic force field. This demonstrates the greater power of the traditional perturbation approach of Mills and Robiette. Expressions of this work present the perturbation theory formula for the quartic resonance terms that were presented in table 1 of the paper by Della Valle.

## 2. Derivation

We start with the hamiltonian in dimensionless normal coordinates, with the vibrational hamiltonian written as

$$H_v = H_{20} + H_{30} + H_{40} = \left[ \frac{1}{2} \sum_k \omega_k (p_k^2 + q_k^2) \right] + \left[ \frac{1}{6} \sum_{i, m, n} \phi_{i, m, n} q_i q_m q_n \right] \\ \times \left[ \frac{1}{24} \sum_{k, l, m, n} \phi_{k, l, m, n} q_k q_l q_m q_n + \sum_a B_a p_a^2 \right], \quad (1)$$

where  $p_a$  is the vibrational angular momentum operator. One eliminates  $H_{30}$  by the first contact transformation, giving an effective hamiltonian [11]

$$\tilde{H}_v = \frac{1}{2} \sum_k \omega_k (p_k^2 + q_k^2) + \frac{1}{24} \sum_{k, l, m, n} \phi_{k, l, m, n} q_k q_l q_m q_n + \sum_a B_a p_a^2 \\ - \frac{1}{8} \sum_{k, l, m, n, r} \phi_{k, n, r} \phi_{k, l, m} \Omega_{k, l, m}^{-1} [\omega_k \omega_l \omega_m (q_n q_r p_l p_m + p_l p_m q_n q_r + \frac{2}{3} \delta_{m, r} \delta_{n, l}) \\ + \omega_k (\omega_l^2 + \omega_m^2 - \omega_k^2) q_l q_m q_n q_r], \quad (2)$$

with  $\Omega_{i, m, n}$  given by

$$\Omega_{i, m, n} = (\omega_l + \omega_m + \omega_n)(\omega_l + \omega_m - \omega_n)(\omega_l - \omega_m + \omega_n)(-\omega_l + \omega_m + \omega_n). \quad (3)$$

If one has a Fermi resonance interaction ( $\omega_a \cong \omega_b + \omega_c$ ) then one should retain the resonant contribution of the term  $\phi_{abc} q_a q_b q_c$  in the zeroth order hamiltonian, and the terms with  $\Omega_{abc}$  will not appear in the fourth sum for  $H_v$ . The diagonal elements of the above operator give the tradition expression for the energy levels in terms of the harmonic and anharmonic ( $x_{ij}$ ) constants. If, however, we have two frequencies that are nearly degenerate then off diagonal elements from the effective hamiltonian need to be included explicitly, since we then have a case of quasi-degenerative

perturbation theory. It often happens that the harmonic frequencies are not very close to resonant. But as one goes up in excitation, particularly for the overtones of an  $X$ -H stretching mode, the effective stretching frequency falls, tuning different modes into resonance. This quartic hamiltonian will in general connect any states of the same symmetry that differ by two or four quanta, but not three. Since the diagonal elements now contain corrections due to anharmonicity, one has the possibility of treating the low order resonances in this way.

To complement the work of Della Valle, we will now give the full second order perturbation theory expression for the matrix elements that he listed in his table 1. We do not, however, adopt his notation since the use of  $K_{ijkl}$  is more consistent with the work of Mills and Robiette. This represents all possible 1-1 and 2-2 couplings.

$$\langle n_a + 1, n_b - 1, n_c | \tilde{H}_v | n_a, n_b, n_c \rangle = \frac{1}{4} \left[ K_{aaab}(n_a + 1) + K_{abbb}n_b + \sum_{c \neq a, b} 2K_{acbc}(n_c + \frac{1}{2}) \right] \sqrt{[(n_a + 1)n_b]} \quad (4)$$

$$\langle n_a + 2, n_b - 2 | \tilde{H}_v | n_a, n_b \rangle = \frac{1}{4} K_{aabb} \sqrt{[(n_a + 1)(n_a + 2)n_b(n_b - 1)]} \quad (5)$$

$$\langle n_a + 2, n_b - 1, n_c - 1 | \tilde{H}_v | n_a, n_b, n_c \rangle = \frac{1}{4} K_{aabc} \sqrt{[(n_a + 1)(n_a + 2)n_b n_c]} \quad (6)$$

$$\langle n_a + 1, n_b + 1, n_c - 1, n_d - 1 | \tilde{H}_v | n_a, n_b, n_c, n_d \rangle = \frac{1}{4} K_{abcd} \sqrt{[(n_a + 1)(n_b + 1)n_c n_d]} \quad (7)$$

Table 1. Prediction of HCN and DCN spectroscopic constants from HCN coupled morse potential.

	Wavenumbers in $\text{cm}^{-1}$	
	HCN	DCN
$\omega_1$	3437.673	2708.633
$\omega_2$	2130.307	1947.830
$X_{11}$	-51.155	-20.840
$X_{12}$	-14.298	-32.701
$X_{22}$	-11.419	-7.139
$K_{1112}$	65.043	44.612
$K_{1122}$	-0.017	41.436
$K_{1222}$	-44.491	-6.737

Calculated from:

$$\begin{aligned} f_{rr}/aJ \text{ \AA}^{-2} & \quad 6.210, \\ a_r/\text{ \AA}^{-1} & \quad 1.727, \\ f_{RR}/aJ \text{ \AA}^{-2} & \quad 18.809, \\ a_R/\text{ \AA}^{-1} & \quad 2.363, \\ f_{rR}/aJ \text{ \AA}^{-2} & \quad -0.280\dagger, \\ \text{with} & \end{aligned}$$

$$\begin{aligned} V(r, R) = & \frac{f_{rr}}{2a_r^2} [1 - \exp(-a_r r)]^2 + \frac{f_{RR}}{2a_R^2} [1 - \exp(-a_R R)] \\ & + \frac{f_{rR}}{a_r a_R} [1 - \exp(-a_r r)][1 - \exp(-a_R R)]. \end{aligned}$$

$r$  = C-H stretch,  $R$  = C-N stretch,

† This value was incorrectly listed by Baggott, Caldow and Mills. This is the correct value for their fit.

where the anharmonic constants are given by

$$K_{aabb} = \frac{1}{4}\phi_{aabb} + \sum_{\alpha} -B_{\alpha}(\zeta_{ab}^{\alpha})^2 \frac{(\omega_a + \omega_b)^2}{\omega_a \omega_b} \\ + \sum_k \frac{1}{8}\phi_{kaa} \phi_{kbb} \omega_k \times \left[ \frac{1}{4\omega_a^2 - \omega_k^2} + \frac{1}{4\omega_b^2 - \omega_k^2} \right] \\ + \sum_k -\frac{1}{2}\phi_{kab}^2 \frac{\omega_k}{\omega_k^2 - (\omega_a - \omega_b)^2}, \quad (8)$$

$$K_{aaab} = K_{baaa} = \frac{1}{2}\phi_{aaab} + \sum_k -\frac{1}{4} \frac{\phi_{kab} \phi_{kaa}}{\omega_k} \left[ \frac{8\omega_a^2 - 3\omega_k^2}{4\omega_a^2 - \omega_k^2} \right] \\ + \sum_k -\frac{1}{4}\phi_{kab}^2 \omega_k \Omega_{kab}^{-1} (3\omega_a^2 + 3\omega_b^2 + 2\omega_a \omega_b - 3\omega_k^2), \quad (9)$$

$$K_{acbc} = \frac{1}{2}\phi_{abcc} + \sum_{\alpha} 2B_{\alpha} \zeta_{ac}^{\alpha} \zeta_{bc}^{\alpha} \frac{\omega_a \omega_b + \omega_c^2}{\omega_c \sqrt{(\omega_a \omega_b)}} \\ + \sum_k -\frac{1}{4}\phi_{kab}^2 \phi_{kcc} \left[ \frac{1}{\omega_k} + \frac{\omega_k}{\omega_k^2 - (\omega_a - \omega_b)^2} \right] \\ + \sum_k -\frac{1}{2}\phi_{kac} \phi_{kbc} \omega_k \left[ \frac{\omega_a^2 + \omega_c^2 - \omega_k^2}{\Omega_{kac}} + \frac{\omega_b^2 + \omega_c^2 - \omega_k^2}{\Omega_{kbc}} \right], \quad (10)$$

$$K_{aabc} = \frac{1}{2}\phi_{aabc} + \sum_{\alpha} -2B_{\alpha} \zeta_{ab}^{\alpha} \zeta_{ac}^{\alpha} \frac{(\omega_a + \omega_b)(\omega_a + \omega_c)}{\omega_a \sqrt{(\omega_b \omega_c)}} \\ + \sum_k -\phi_{kaa} \phi_{kbc} \omega_k \left[ \frac{1}{\omega_k^2 - (\omega_b + \omega_c)^2} + \frac{1}{\omega_k^2 - 4\omega_a^2} \right] \\ + \sum_k -2\phi_{kab} \phi_{kac} \omega_k \left[ \frac{1}{\omega_k^2 - (\omega_a - \omega_c)^2} + \frac{1}{\omega_k^2 - (\omega_a - \omega_b)^2} \right], \quad (11)$$

$$K_{abcd} = \phi_{abcd} + \sum_{\alpha} 2 \frac{B_{\alpha}}{\sqrt{(\omega_a \omega_b \omega_c \omega_d)}} [\zeta_{ab}^{\alpha} \zeta_{cd}^{\alpha} (\omega_a - \omega_b)(\omega_c - \omega_d) \\ - \zeta_{ac}^{\alpha} \zeta_{ad}^{\alpha} (\omega_a + \omega_c)(\omega_b + \omega_d) - \zeta_{ad}^{\alpha} \zeta_{bc}^{\alpha} (\omega_a + \omega_d)(\omega_b + \omega_c)] \\ \times \sum_k -\frac{1}{2}\phi_{kab} \phi_{kcd} \omega_k \left[ \frac{1}{\omega_k^2 - (\omega_a + \omega_b)^2} + \frac{1}{\omega_k^2 - (\omega_c + \omega_d)^2} \right] \\ + \sum_k -\frac{1}{2}\phi_{kac} \phi_{kbd} \omega_k \left[ \frac{1}{\omega_k^2 - (\omega_a - \omega_c)^2} + \frac{1}{\omega_k^2 - (\omega_b - \omega_d)^2} \right] \\ + \sum_k -\frac{1}{2}\phi_{kad} \phi_{kbc} \omega_k \left[ \frac{1}{\omega_k^2 - (\omega_a - \omega_d)^2} + \frac{1}{\omega_k^2 - (\omega_b - \omega_c)^2} \right]. \quad (12)$$

The constant  $K_{aabb}$  is the Darling-Dennison constant, and the present formulae agree with those given earlier by Mills and Robiette if one takes  $\omega_a = \omega_b = \omega_{ab}$  as was done in their formula. The present formulae are very similar to those that determine the  $x_{ij}$  constants, as they should be since they derive from the diagonal and off-diagonal terms of the same operator.

The present formulae apply to both nondegenerate and degenerate modes, although for the latter one must explicitly use the complete set of degenerate modes.

For the common case of doubly degenerate modes, one can recover expressions in the more traditional quantum numbers  $|n_i, l_i\rangle$  if one uses in the anharmonic expansion the coordinates

$$q_{i\pm} = \frac{1}{\sqrt{2}}(q_a \pm iq_b) \quad (13)$$

and then makes the substitution

$$n_i = n_{i+} + n_{i-}, \quad \ell_i = n_{i+} - n_{i-}. \quad (14)$$

The use of quantum numbers  $|n_i, \ell_i\rangle$  makes the formula for degenerate and non-degenerate modes different, and does not appear to have anything to recommend it except tradition. It is important however, not to use the  $q_a$  and  $q_b$  normal modes since they lack the full symmetry of the molecule.

### 3. Test calculations

As an example to show the practical usefulness of these formulae, consider a simple problem of two coupled Morse oscillators. We will use the parameters recently determined by Baggott, Caldow and Mills [12] in their fit of the spectrum of HCN and DCN using the modified AACAO method. For DCN, the C-D and CN modes are nearly resonant, and the normal modes strongly mixed. Thus, one would expect that the present approach would be significantly better than a traditional anharmonic expansion in terms of  $\omega_i$  and  $X_{ij}$ . For HCN, the normal modes are much closer to pure CH and CN motions, and the frequencies are far from a one-one resonance. However, as one goes up the C-H overtone ladder the effective C-H frequency drops, leading to stronger interaction. The present approach allows for such increased delocalization at higher energy.

In order to test the accuracy of the new approach, we have first calculated the vibrational term values variationally for the potential of Baggott, Caldow and Mills using a basis set of products of Morse oscillator wavefunctions for the C-H and C-N bond modes [13]. All basis states with diagonal energy  $< 50\,000\text{ cm}^{-1}$  were used (240 states for HCN, 330 states for DCN). We expect that the calculated eigenstates up to  $20\,000\text{ cm}^{-1}$  are much more accurate than an anharmonic expansion, so we will treat them as essentially the exact eigenvalues for the problem.

Using the traditional perturbation formula and the expressions given above, we have calculated the constants  $\omega_i$ ,  $X_{ij}$ ,  $K_{1112}$ ,  $K_{1122}$ , and  $K_{1222}$  for both HCN and DCN from the potential. These are given in table 1 along with the parameters used.  $\omega_1$  corresponds to the mode  $v_3$  in the traditional mode assignments of H(D)CN, while  $\omega_2$  corresponds to  $v_1$ . For the anharmonic expansion, the energy levels were calculated, relative to the ground state by

$$E(n_1, n_2) = \omega_1 n_1 + \omega_2 n_2 + X_{11} n_1 (n_1 + 1) \\ + X_{12} (n_1 n_2 + \frac{1}{2} n_1 + \frac{1}{2} n_2) + X_{22} n_2 (n_2 + 1). \quad (15)$$

For the anharmonic resonance hamiltonian, we must diagonalize the  $(n+1)$  dimensional submatrix of all basis states where  $n_1 + n_2 = n$ , with the off diagonal terms connecting the state  $|n_1, n_2\rangle$  with  $|n_1 \pm 1, n_2 \mp 1\rangle$  ( $K_{1222}$  and  $K_{1112}$ ) and  $|n_1 \pm 2, n_2 \mp 2\rangle$  ( $K_{1122}$ ) as given earlier. For the sake of comparison, we have also calculated the energy levels using the revised AACAO model. This model has matrix

Table 2. Vibrational energy term values, in  $\text{cm}^{-1}$ , for stretching overtone states. DCN

State	Variational energy	Anharmonic expansion - variational	Anharmonic expansion and K1222 + K1112, K1122 - variational	Revised AACAO - variational
(0, 1)	1917.049	0.153	0.030	+3.755
(1, 0)	2650.726	-0.123	-0.001	-2.519
(0, 2)	3819.626	0.499	0.044	7.404
(1, 1)	4533.963	1.141	0.114	2.160
(2, 1)	5261.067	-1.540	-0.058	-5.694
(0, 3)	5707.734	1.037	-0.015	10.912
(1, 2)	6402.251	3.076	0.396	6.556
(2, 1)	7109.818	1.509	-0.023	0.129
(3, 0)	7832.132	-5.361	-0.099	-9.491
(0, 4)	7581.371	1.767	-0.200	14.244
(1, 3)	8255.607	5.664	0.712	10.568
(2, 2)	8942.953	5.895	0.721	5.511
(3, 1)	9645.945	-0.076	-0.791	-2.198
(4, 0)	10364.956	-12.622	0.188	-13.909
(0, 5)	9440.527	2.700	-0.565	17.481
(1, 4)	10094.035	8.903	0.930	13.907
(2, 3)	10760.497	11.595	0.098	10.220
(3, 2)	11443.335	7.355	0.405	4.704
(4, 1)	12143.571	-4.839	-0.984	-4.728
(5, 0)	12860.499	-24.281	1.547	-19.008
(0, 6)	11285.190	3.848	-1.166	+20.889
(1, 5)	11917.519	12.086	0.701	16.275
(2, 4)	12562.438	18.619	-2.573	13.723
(3, 3)	13224.361	16.871	-36.265	10.666
(4, 2)	13904.845	6.006	-2.923	4.480
(5, 1)	14603.807	-13.893	-14.417	-7.362
(6, 0)	15319.634	-41.212	+59.690	-24.950

Level (3, 3) and (6, 0) DO NOT appear to be involved with interband resonance based upon the value of  $\langle N_1 + N_2 \rangle$  calculated from the variational wavefunction.

elements of similar form, but is based upon perturbations away from uncoupled bond modes.

Tables 2 and 3 gives the results for DCN and HCN, respectively. The first column gives the quantum number assignments with  $\nu_1$  being the 'C-D(H)' stretch and  $\nu_2$  being the 'C-N' stretch. The second column gives the energies calculated variationally. The third, the difference between the state energy calculated by the anharmonic expansion (equation (15)) and the variational energy. As discussed above, we assign most of the discrepancy as being due to errors in anharmonic expansion. The fourth column gives an analogous comparison with prediction, including the (1-1) and (2-2) anharmonic resonance terms. The last column gives the comparison with the modified AACAO model.

The results for DCN show the importance of including the resonance terms. For all the blocks with  $n \leq 5$ , the errors are typically one order of magnitude less than those without them. In the  $n = 6$  block, two states stick out, the (3, 3) and (6, 0), with anomalously large errors. An obvious guess is that they may be in resonance

Table 3. Vibrational energy term values, in  $\text{cm}^{-1}$ , for stretching overtone states. HCN.

State	Variational energy	Anharmonic expansion - variational	Anharmonic expansion and K1222 + K1112, K1122 - variational	Revised AACAO - variational
(0, 1)	2100·226	-0·016	0·072	+1·181
(1, 0)	3328·342	--0·128	--0·107	--0·180
(0, 2)	4177·617	0·184	0·126	+1·560
(1, 1)	5413·176	1·059	0·314	+3·430
(2, 0)	6555·662	-1·545	-0·742	-1·481
(0, 3)	6232·089	0·354	-0·351	+1·007
(1, 2)	7475·461	1·957	2·294	+6·810
(2, 1)	8623·404	2·437	-1·225	+3·829
(3, 0)	9683·591	-5·880	-1·850	-3·749
(0, 4)	8263·587	0·659	-1·879	-0·641
(1, 3)	9514·930	2·832	5·366	+10·010
(2, 2)	10669·197	5·528	1·541	+9·225
(3, 1)	11731·893	3·243	-4·710	+2·605
(4, 0)	12715·341	-16·347	-4·404	-7·885
(0, 5)	10272·083	1·127	-4·981	--3·533
(1, 4)	11531·360	3·907	9·029	+12·923
(2, 3)	12691·496	9·275	8·250	+16·147
(3, 2)	13759·076	10·646	-2·400	9·081
(4, 1)	14741·729	0·392	-12·051	-1·622
(5, 0)	15649·484	--31·518	--4·019	--9·498
(0, 6)	12257·590	1·746	-10·194	-7·825
(1, 5)	13524·546	5·387	12·778	+15·486
(2, 4)	14691·534	12·444	16·786	+22·883
(3, 3)	15765·377	16·093	3·944	+15·632
(4, 2)	16747·874	14·535	-12·265	+4·439
(5, 1)	17646·220	0·575	-14·801	+0·040
(6, 0)	18494·404	--59·775	-5·243	-13·237

with states from other 'blocks'. However, the expectation value for the sum of number operators  $N_{\text{CH}} + N_{\text{CN}}$  (Morse basis number operators) is 6·07 for the (3, 3) state and 6·05 for the (6, 0) state, while 6·06 for the (4, 2) state, indicating that interblock resonance is not a significant factor in the above discrepancies. Perhaps a sextic interaction is responsible, since that will have terms that push the (3, 3) and (6, 0) apart, but it is not clear why it would have an important effect on just these two levels. The modified AACAO predictions are clearly inferior, due perhaps to the normal modes being strongly mixed combinations of the bond modes.

The results for HCN show only modest improvement when the resonance interactions are included. The only substantial improvement are in the energy levels ( $n, 0$ ), which have by far the largest errors when the resonance terms are not included, though that improvement appears to cause the ( $n - 1$ ) levels to become much more poorly predicted than before. It is interesting to note that a similar trend of errors is observed in an anharmonic fit to the observed HCN spectrum [14]. Adding a  $y_{333}$  term to the fitting hamiltonian improves the fit of the (0, 0,  $n$ ) levels, but at the cost of increased residuals for the (1, 0,  $n - 1$ ). It should be noted that in

HCN, the modes  $\nu_3$  and  $\nu_1$  are close to being in 2-3 resonance, which connects states of different blocks, so the very modest improvement of our current treatment for HCN should not be unexpected. However, Caldow and Mills [5] did have success with fitting the HCN spectrum with a Child and Lawton type of hamiltonian. Translated to a normal mode basis this hamiltonian would be of the form we are using, but with relations between the  $X_{ij}$ s and  $K_{ijkl}$ s. The present results, however, strongly suggest that the success of their model at fitting the HCN spectrum should not be mistaken as implying the accuracy of such a simple hamiltonian for HCN. It is interesting to note that the predictions of the AACAO model are somewhat worse for the lower blocks; the two models do about equally well for predictions on the  $n = 6$  block. It is also noted that errors for the states  $(0, n)$  are not particularly large, in contrast to the expectation of Baggott *et al.* In deriving the AACAO model, certain approximations were made to simplify the form of the matrix elements. It would be very interesting to have a comparison without these approximations.

#### 4. Conclusion

We have extended the earlier work of Mills and Robiette, and have found the full perturbation theory expression for all 1-1 resonance interactions, up to quartic terms in the hamiltonian. These expressions can be used directly to predict an overtone spectrum from a model quartic potential. They can also be used to check the accuracy of 'x-K' relations derived using the algebraic methods used for equivalent bond modes, but also applicable to nonequivalent bonds.

The present formulae have been used to predict the stretching vibrations of a physically realistic model hamiltonian for DCN and HCN. The accuracy of the predictions improved dramatically for most of the levels of DCN, but only makes a substantial improvement for the pure C-H overtone states of HCN. We expect that these terms will be important in the overtone spectrum of many molecules, especially those with inequivalent hydrogen atoms, or with partial deuterium substitutions.

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