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On the relationship of normal modes to local modes in molecular vibrations

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A simple model for the effective vibrational hamiltonian of the XH stretching vibrations in H₂O, NH₃ and CH₄ is considered, based on a morse potential function for the bond stretches plus potential and kinetic energy coupling between pairs of bond oscillators. It is shown that this model can be set up as a matrix in local mode basis functions, or as a matrix in normal mode basis functions, leading to identical results. The energy levels obtained exhibit normal mode patterns at low vibrational excitation, and local mode patterns at high excitation. When the hamiltonian is set up in the normal mode basis it is shown that Darling–Dennison resonances must be included, and simple relations are found to exist between the $x_{rs}, g_{n},$ and $K_{res}$ anharmonic constants (where the Darling–Dennison coefficients are denoted $K$) due to their contributions from morse anharmonicity in the bond stretches. The importance of the Darling–Dennison resonances is stressed. The relationship of the two alternative representations of this local mode/normal mode model are investigated, and the potential uses and limitations of the model are discussed.

1. INTRODUCTION

Local modes are now well accepted as providing a model for highly excited stretching vibrational states in molecules, for which they usually give a closer representation of the true situation than the traditional picture of multiple excitation of the normal vibrations. The subject has been fully reviewed by Child and Halonen [1], where many references to the recent literature on local modes may be found.

For molecules containing symmetrically equivalent sets of stretching vibrations, such as H₂O, NH₃, or CH₄, quite different forms are predicted for the classical vibrations and for the quantum mechanical wavefunctions by the local mode and normal mode models. The truth should be understood as something between the limiting situation represented by either model, as determined by the competition between morse-like anharmonicity (which favours the local mode picture) and kinetic and potential coupling between the local bond oscillators (which favours the normal mode picture). As the stretching vibrations become more highly excited, the morse anharmonicity associated with the approach towards bond dissociation tends to dominate, and thus the local mode model...
In practice it is found that even 2 or 3 quanta of stretching vibrational energy (equivalent to only about 15 per cent of the energy required for dissociation of an X–H bond) may be sufficient to bring the true vibrational wavefunctions closer to the local mode than the normal mode limit.

This picture of the true situation as a compromise between the two limiting models, depending on the relative magnitudes of morse anharmonicity and inter-bond coupling, is nicely illustrated by the correlation diagrams between normal and local mode limits shown in Child and Halonen's review [1]. An example of such a diagram for XH₂ molecules is reproduced in figure 2 in §3 below.

The mathematical formulation of the problem is usually presented by setting up a hamiltonian matrix in a set of local mode basis functions, and introducing the effects of interbond coupling as off-diagonal interactions in the matrix. The preceding discussion, however, suggests that it should be possible to find an equivalent formulation in terms of normal mode basis functions in which the effects of morse anharmonicity are introduced as the perturbing effect. This paper is concerned with developing the equivalence between these two alternative formulations, and understanding more fully the transformation between the two sets of basis functions. Lehmann [2] has already shown how the two approaches may be related in the case of two equivalent bond oscillators, as in the H₂O molecule. This paper is closely related to his work, although our work was done independently. We extend the relationship to three and four equivalent bond oscillators and provide some further insight into the nature of the models involved. As Lehmann has observed, a particular feature of the mathematical formulation in terms of normal mode basis functions is the need to include the effects of Darling-Dennison resonances between overtone levels [3]; these provide the anticipated off diagonal terms due to morse anharmonicity in the normal mode basis. Accordingly we include some discussion of these effects and develop formulae for Darling-Dennison resonance terms in the effective vibrational hamiltonian of NH₃ and CH₄ type molecules.

The mathematical formulation in this paper is based on morse potential functions for the bond stretching coordinates. Although this is well known to be an imperfect approximation to the stretching potential functions of real molecules, it is analytically convenient, and the resulting effective hamiltonians give a remarkably good fit to the known data on vibrational overtone energy levels. As discussed later, the essential ideas involved are not sensitive to the precise shape of the bond potential function at the approach to dissociation.

This paper is arranged as follows. In §2 we review some of the properties and formulae for the morse diatomic oscillator. In §§3, 4 and 5 we discuss the development of effective vibrational hamiltonians for molecules with two, three and four bond oscillators respectively (e.g. H₂O, NH₃ and CH₄ type molecules). Section 6 is a brief review, with a discussion of the importance of the formulation in terms of normal mode basis functions for future work. Finally in the appendix we present some general formulae for Darling-Dennison resonance terms in H₂O, NH₃ and CH₄ type molecules.

2. The diatomic morse oscillator

The morse oscillator potential function is defined by the formula

\[ V_m(r) = D_e[1 - \exp (-ar)]^2, \]  

(1)
where $r$ is the displacement from equilibrium in the bond stretching coordinate, $D_e$ is the dissociation energy from equilibrium, and the parameter $a$ determines the harmonic force constant around equilibrium. It is thus a two parameter function: the shape of the potential is determined by the parameters $D_e$ and $a$. Adding the kinetic energy gives the hamiltonian of a diatomic Morse oscillator

$$H = \frac{1}{2} g_{rr} \dot{r}^2 + D_e [1 - \exp (-a r)]^2,$$

where the momentum $\dot{r} = -i\hbar \frac{\partial}{\partial r}$, and $g_{rr}$ is the reciprocal effective mass, or $g$ matrix element [4], given by $g_{rr} = (1/m_x + 1/m_y)$ for an XH diatomic molecule. It is well known that this hamiltonian can be solved exactly analytically† giving vibrational term values

$$G(v) = E(v)/\hbar c = \omega(v + \frac{1}{2}) + x(v + \frac{1}{2})^2.$$

We have written $\omega$ and $x$ for the harmonic wavenumber and the anharmonicity constant, which are usually written $\omega_x$ and $-\omega_x x_x$; this change from the customary diatomic notation is made to draw the analogy with the notation for polyatomic molecules used below. The harmonic wavenumber and the anharmonicity constant are related to the parameters in the hamiltonian by the equations

$$\omega = \hbar (2a^2 D_e g_{rr})^{1/2}/\hbar c,$$

$$x = -a^2 \hbar^2 g_{rr}/2\hbar c.$$

† See the discussion in Child and Halonen [1] for further references and formulae. A very small approximation is involved in applying the boundary condition at zero bond distance, $r = -r_e$. 

Figure 1. The Morse function, compared with the harmonic potential obtained from its leading quadratic term. The parameters are approximately adjusted to fit the OH bond in the $\text{H}_2\text{O}$ molecule ($1\text{Å} = 0.1\text{nm}$).
Typical values of $D_e$ and $a$ for XH diatomics are $D_e \approx 1 \text{ aJ} \approx \hbar c (50000 \text{ cm}^{-1})$, and $a \approx 2 \text{ Å}^{-1}$, giving $\omega \approx 3500 \text{ cm}^{-1}$ and $x \approx -80 \text{ cm}^{-1}$. Figure 1 shows a morse potential approximately adjusted to these values.

The above formulae may be obtained by an alternative route, which is interesting because of its relation to the formulation of local modes in terms of normal mode basis functions in the following sections. Expanding (1) about the equilibrium $r = 0$ gives

$$V_m(r) = \frac{1}{2} f_{rr} r^2 + (1/6) f_{rrr} r^3 + (1/24) f_{rrrr} r^4 + \ldots,$$

(6)

where the quadratic, cubic and quartic force constants are easily found to be given by

$$f_{rr} = (\partial^2 V/\partial r^2)_0 = 2a^2 D_e,$$

(7)

$$f_{rrr} = (\partial^3 V/\partial r^3)_0 = -6a^3 D_e = -3af_{rr},$$

(8)

$$f_{rrrr} = (\partial^4 V/\partial r^4)_0 = 14a^4 D_e = 7a^2 f_{rr}.$$  

(9)

For small displacements one may usefully neglect fifth and higher power terms, and treat the cubic and quartic terms by perturbation theory, applied to the solutions of a zeroth order harmonic oscillator hamiltonian based on the quadratic potential only. The algebra is as follows:

$$H = H^0 + H^{'},$$

(10)

$$H^0 = \frac{1}{2} g_{rr} p_r^2 + \frac{1}{2} f_{rr} r^2$$

(11a)

$$= \frac{1}{2} \hbar c \omega (p^2 + q^2),$$

(11b)

$$H^{'} = (1/6) f_{rr} r^3 + (1/24) f_{rrr} r^4$$

(12a)

$$= \hbar c [(1/6) \phi_3 q^3 + (1/24) \phi_4 q^4].$$

(12b)

In (11b) and (12b) the hamiltonian has been re-expressed in terms of the usual dimensionless coordinate $q$ ($q = \pm 1$ at the classical turning points in the ground vibrational state) and its dimensionless conjugate momentum $\tilde{p} = -i \hbar \partial / \partial q$. $\phi_3$ and $\phi_4$ are the cubic and quartic anharmonic force constants for the coordinate $q$, in wavenumber units, following the notation of Hoy, Mills and Strey [5]. The necessary relations are

$$q = \alpha^{1/2} r, \quad \alpha = 2\pi c \omega / \hbar g_{rr},$$

(13)

$$\omega = (g_{rr} f_{rr})^{1/2} / 2\pi c = (2a^2 D_e g_{rr})^{1/2} / 2\pi c,$$

(14)

$$\phi_3 = f_{rr} / \hbar c \alpha^{3/2}, \quad \phi_4 = f_{rrr} / \hbar c \alpha^2.$$  

(15)

Treating $H^{'}$ by perturbation theory, using second order perturbation theory for the cubic term and only first order for the quartic term, we arrive at the eigenvalue expression

$$E(v)/\hbar c = G(v) = \omega(v + \frac{1}{2}) + x(v + \frac{1}{2})^2,$$

(16)

exactly as in equation (3). The anharmonicity constant $x$ is obtained from the perturbation treatment as

$$x = \phi_4 / 16 - 5 \phi_3^2 / 48 \omega.$$  

(17)

Finally, using equations (13), (14) and (15), and (8) and (9), to eliminate $\phi_3$, $\phi_4$ and $\omega$ in terms of the morse parameters, we recover equation (5) for $x$. Thus the
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perturbation theory expression for the energy levels in (16) is identical to the exact solution given in equation (3).

It seems at first surprising that the perturbation treatment with all its approximations should reproduce the exact solution. No higher than quartic terms in the potential have been considered, and truncation at the quartic term gives a potential which deviates seriously from the morse curve above \( v = 4 \), as shown in figure 1. The explanation is that inclusion of higher terms in the polynomial, and extending the theory to higher orders of perturbation theory, does not change the formulae obtained for \( \omega \) and \( \chi \); instead it adds higher terms to the expansion in \( (v + \frac{1}{2}) \) in (16), such as \( y(v + \frac{1}{2})^3 \). However we know that in the final analysis all such terms will prove to be zero. Hence the limited perturbation analysis described above reproduces the exact result.

In the following sections we consider the analogous perturbation treatment of the stretching vibrations in some simple polyatomic molecules. Although there is no exact analytical solution for the polyatomics, it seems likely that the anharmonic vibrational energy levels calculated from the perturbation treatment represent the exact solution up to much higher energies than the truncated polynomial representation of the morse potential might suggest, as observed here for a diatomic molecule.

3. **TWO EQUIVALENT BOND OSCILLATORS: H\(_2\)O**

The treatment below will ignore all vibrations in the molecule except the two \( \chi \)H stretching vibrations (although we return to this point in the discussion in §6). It is thus applicable to any molecule with two symmetrically equivalent coupled morse oscillators (such as H\(_2\)C=O, H–C≡C–H, and cis or trans difluoroethene, etc.). We consider two equivalent effective vibrational hamiltonians, in the local mode basis and the normal mode basis respectively.

(i) **The local mode basis**

We consider first an effective vibrational hamiltonian defined by its matrix in a set of local mode basis functions. A typical local mode basis function is denoted \( |m, n\rangle \), corresponding to \( m \) quanta of excitation in bond \( a \) and \( n \) quanta in bond \( b \). (We use the labels \( r_a \) and \( r_b \) for the two bond stretches, reserving the numerical indices \( S_1 \) and \( S_3 \) for the symmetry coordinates defined as in-phase and out-of-phase combinations of the bond stretches.) For a total vibrational excitation of \( v \) quanta, where \( v = m + n \), there are \( v + 1 \) basis functions, and we define the corresponding vibrational energy levels as the eigenvalues of a \( (v + 1) \times (v + 1) \) matrix whose non-zero elements are given by

\[
\langle m, n | H | m, n \rangle = \omega_m(m + n + 1) + x_m[(m + \frac{1}{2})^2 + (n + \frac{1}{2})^2],
\]

\[
\langle m + 1, n - 1 | H | m, n \rangle = \lambda[(m + 1)n]^{1/2},
\]

\[
\langle m - 1, n + 1 | H | m, n \rangle = \lambda[(m(n + 1)]^{1/2}.
\]

We take the matrix to be block diagonal in \( v = m + n \), so that there are no matrix elements connecting blocks corresponding to different values of \( v \). We postpone for later discussion the question of how this matrix is derived, and whether the
basis functions \( |m, n\rangle \) are to be thought of as products of harmonic oscillator or morse oscillator functions.

The parameters in this model have the following significance. \( \omega_m \) and \( x_m \) are the harmonic wavenumber and anharmonicity constant associated with either of the bonds regarded as an independent morse oscillator; they are related to the morse parameters by equations (4) and (5). The subscript \( m \) has been added to emphasize their relation to the morse function of a single bond stretching coordinate. \( \lambda \) represents the inter-bond coupling; we show below that it may be related to the \( f \) matrix and \( g \) matrix coupling terms by the equation

\[
\lambda = (\omega_m/2)[(g_{rr}/g_{rr}) + (f_{rr}/f_{rr})],
\]

Thus if \( \lambda = 0 \), so that all off-diagonal matrix elements are zero, we have independent vibrations in the two bonds, corresponding to a pure local mode model, and the eigenvalues are given by the diagonal matrix elements (18) above. The corresponding energy levels are illustrated on the right hand side of figure 2.

Figure 2. Stretching vibrational energy levels for the water molecule, in a diagrammatic representation. The levels on the left hand side represent the pure normal mode limit, and they are labelled with the quantum numbers \( v_1, v_3 \); the energy levels are given by equation (25) with \( x_m = 0 \). The levels on the right hand side represent the pure local mode limit, and they are labelled with the quantum numbers \( m, n \); the energy levels are given by equation (18). The true energy levels are as sketched in the center of the diagram. They may be obtained either by introducing the effects of the anharmonicity \( x_m \) (including Darling–Dennison resonance) on the left, or by introducing the effects of interbond coupling \( \lambda \) on the right.
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(ii) The normal mode basis

We consider now an effective vibrational hamiltonian defined by its matrix elements in a set of normal mode basis functions $|v_1, v_3\rangle$, where $v_1$ and $v_3$ denote the number of quanta in the two normal vibrations $v_1$ (the symmetric stretch, of symmetry $A_1$) and $v_3$ (the antisymmetric stretch, of symmetry $B_2$) respectively. Once again, for a given total excitation $v = v_1 + v_3$ there are $v + 1$ basis functions, and we take the hamiltonian matrix to be block diagonal in $v$. The non-zero matrix elements are given by the formulae

$$
\langle v_1, v_3 | H/\hbar | v_1, v_3 \rangle = \omega_1 (v_1 + \frac{1}{2}) + \omega_3 (v_3 + \frac{1}{2})
+ x_{11} (v_1 + \frac{1}{2})^2 + x_{33} (v_3 + \frac{1}{2})^2
+ x_{13} (v_1 + \frac{1}{2})(v_3 + \frac{1}{2}),
$$

(21)

$$
\langle v_1 + 2, v_3 - 2 | H/\hbar | v_1, v_3 \rangle = \left(\frac{1}{4}\right) K_{1133}
\times [(v_1 + 1)(v_1 + 2)v_3(v_3 - 1)]^{1/2} \quad (22a)
$$

$$
\langle v_1 - 2, v_3 + 2 | H/\hbar | v_1, v_3 \rangle = \left(\frac{1}{4}\right) K_{1133}
\times [v_1(v_1 - 1)(v_3 + 1)(v_3 + 2)]^{1/2}. \quad (22b)
$$

Equation (21) is the customary expression for the anharmonic corrections to the energy levels in a polyatomic molecule with two normal modes of vibration. Equations (22) describe the Darling-Dennison resonance interaction between overtones of $v_1$ and $v_3$ [3]. (The coefficient $K_{1133}$ used here is related to the coefficient $\gamma$ used in Darling and Dennison's paper by $K_{1133} = 2\gamma$.) We also impose the following relations between the parameters in equations (21) and (22). We write

$$
\omega_1 = \omega_m + \lambda, \quad \omega_3 = \omega_m - \lambda
$$

$$
x_{11} = x_{33} = x_{13}/4 = K_{1133}/4 = x_m/2. \quad (23, 24)
$$

The physical significance of the parameters $\omega_m$, $x_m$, and $\lambda$ proves to be exactly as before. The origin of the relations (23) and (24) is discussed below. The matrix elements may thus be rewritten in the form

$$
\langle v_1, v_3 | H/\hbar | v_1, v_3 \rangle = \omega_m (v_1 + v_3 + 1) + \lambda(v_1 - v_3)
+ \frac{1}{2} x_m [(v_1 + \frac{1}{2})^2 + (v_3 + \frac{1}{2})^2]
+ 4(v_1 + \frac{1}{2})(v_3 + \frac{1}{2}),
$$

(25)

$$
\langle v_1 + 2, v_3 - 2 | H/\hbar | v_1, v_3 \rangle = \frac{1}{2} x_m [(v_1 + 1)(v_1 + 2)v_3(v_3 - 1)]^{1/2} \quad (26a)
$$

$$
\langle v_1 - 2, v_3 + 2 | H/\hbar | v_1, v_3 \rangle = \frac{1}{2} x_m [v_1(v_1 - 1)(v_3 + 1)(v_3 + 2)]^{1/2}. \quad (26b)
$$

The hamiltonian matrix expressed here in normal mode basis functions has off-diagonal elements due to the Darling-Dennison terms. If $x_m$ is set to zero, the matrix is diagonal, with eigenvalues given by the first two terms in (25), and we recover the pure normal mode model. The corresponding energy level pattern is shown on the left hand side of figure 2.

Although it is not immediately obvious, it is a fact that the hamiltonian matrix defined in equations (25) and (26) gives the same eigenvalues, except for a small change in the energy zero, as that defined in (18) and (19). The change in the
energy zero is such that the term values obtained from (25) and (26) are all \(x_m/4\) higher† than those from (18) and (19). The two matrices represent the same physical situation in terms of two different basis sets. We call them the local mode and the normal mode representations respectively. The eigenvalues obtained are illustrated qualitatively in the centre of figure 2, which is a correlation diagram between the local mode and normal mode limits.

The equivalence of these two representations may be demonstrated numerically by writing a computer program (which is how we first discovered it). It has also been demonstrated analytically by Lehmann [2], who has determined the general transformation between the two sets of basis functions, following some earlier work of Kellmann [6]. This transformation determines the relation between the eigenvectors of the two matrix representations presented above.

(iii) **The hamiltonian operator**

The reason for this equivalence can be seen physically by considering the hamiltonian operator which gives rise to these matrices. We start from a zero order hamiltonian which is simply two uncoupled harmonic oscillators in the bond displacement coordinates \(r_a\) and \(r_b\):

\[
H^0 = \frac{1}{2}g_{rr}(\dot{r}_a^2 + \dot{r}_b^2) + \frac{1}{2}f_{rr}(r_a^2 + r_b^2). \tag{27}
\]

To this we add two perturbations: the first, \(H'_1\), converts the potential terms in \(H^0\) from harmonic to morse form; and the second, \(H'_2\), adds the required interbond potential and kinetic coupling.

\[
H'_1 = -\frac{1}{2}f_{rr}(r_a^2 + r_b^2) + V_m(r_a) + V_m(r_b), \tag{28}
\]

\[
H'_2 = g_{rr}\dot{r}_a\dot{r}_b + f_{rr}r_ar_b. \tag{29}
\]

Here \(V_m(r)\) is the morse function defined in equation (1), and the first term in (28), with coefficient \(-\frac{1}{2}f_{rr}\), cancels the leading quadratic terms in the polynomial expansions of the morse functions. The coefficients \(g_{rr'}\) and \(f_{rr'}\) in (29) are the usual quadratic \(g\) matrix and \(f\) matrix coupling terms.

To see how this gives the local mode matrix, we take the local mode basis functions \(|m, n\rangle\) to be eigenfunctions of \(H^0\) in (27), in the form of products of harmonic oscillator functions of \(r_a\) and \(r_b\). \(H'_1\) in (28) has only diagonal matrix elements within a given \(v = m + n\) block, but it has off-diagonal elements between different blocks satisfying \(\Delta m = \pm 1, \pm 3\) with \(\Delta n = 0\), and \(\Delta m = 0\) with \(\Delta n = \pm 1, \pm 3\). If these are treated by perturbation theory in a manner similar to that described in the last section for a single morse oscillator, the off-diagonal elements with \(\Delta v \neq 0\) may be eliminated to give an effective hamiltonian matrix for which the diagonal matrix elements of \(H^0 + H'_1\) within each \(v\) block are those given in equation (18). Finally \(H'_2\) in (29) can be written in the form

\[
H'_2 = \hbar c^2\omega_m[g_{rr}/g_{rr'}]\dot{q}_a\dot{q}_b + (f_{rr'}/f_{rr})q_aq_b, \tag{30}
\]

where we have transformed to the dimensionless coordinates \(q_a\) and \(q_b\) and the conjugate dimensionless momenta \(\dot{q}_a\) and \(\dot{q}_b\) in place of \(r_a\) and \(r_b\), using the

† Since \(x\) is negative, it might be better to say that the eigenvalues obtained from (18) and (19) are all \(x_m/4\) higher than those from (25) and (26).
transformation in equations (13). It is now easily seen that $H_2$ gives the matrix elements in (19), where $\lambda$ is as defined in equation (20).

To obtain the normal mode matrix is a little more complex. We first transform the hamiltonian from its expression in terms of $r_a$ and $r_b$ to the usual symmetry coordinates $S_1$ and $S_3$, defined by

$$ S_1 = (r_a + r_b)/\sqrt{2}, \quad S_3 = (r_a - r_b)/\sqrt{2}. \quad (31) $$

This gives

$$ H^0 = \frac{1}{2}(g_{rr} \tilde{P}_{S_1}^2 + f_{rr} S_1^2) + \frac{1}{2}(g_{rr} \tilde{P}_{S_3}^2 + f_{rr} S_3^2), \quad (32) $$

$$ H'_1 = \frac{1}{6}F_{111}S_1^3 + \frac{1}{4}F_{133}S_1S_3^2 \quad + \frac{1}{24}F_{333}S_3^4 + \frac{1}{24}F_{333}S_3^2, \quad (33) $$

$$ H'_2 = \frac{1}{6}[g_{rr}(\tilde{F}_S^1 - \tilde{F}_S^3) + f_{rr}(S_1^2 - S_3^2)] \quad (34) $$

In (33) we have expanded the morse function, retained only the cubic and quartic terms, and transformed these into symmetry coordinates. The constants $F_{ijk}$ and $F_{ijk}'$ are related to $f_{rr}$ and $f_{rr}'$ by the equations

$$ F_{111} = F_{133} = f_{rr}/\sqrt{2}, \quad F_{111} = F_{133} = F_{333} = f_{rr}/2. \quad (35) $$

The final step is to transform to dimensionless normal coordinates and momenta, $q_1$ and $q_3$, related to $S_1$ and $S_3$ by the usual equations $q_1 = \alpha^{1/2} S_1$, $q_3 = \alpha^{1/2} S_3$. This gives

$$ H^0/\hbar c = \frac{1}{2}\omega_m(\tilde{p}_1^2 + q_1^2) + \frac{1}{2}\omega_m(\tilde{p}_3^2 + q_3^2), \quad (36) $$

$$ H'_1/\hbar c = \frac{1}{6}\phi_{111}q_1^3 + \frac{1}{4}\phi_{133}q_1q_3^2 \quad + \frac{1}{24}\phi_{333}q_3^4 \quad + \frac{1}{24}\phi_{333}q_3^2, \quad (37) $$

$$ H'_2/\hbar c = \frac{1}{6}[g_{rr}/g_{rr}'(\tilde{p}_1^2 - \tilde{p}_3^2) + (f_{rr}/f_{rr}')q_1^2 - q_3^2], \quad (38) $$

where the force constants $\phi$ are given by

$$ \phi_{111} = \phi_{133} = F_{111}/\hbar c^{3/2} = f_{rr}/\sqrt{2}\hbar c^{3/2}, \quad (39) $$

$$ \phi_{111} = \phi_{133} = \phi_{333} = F_{1111}/\hbar c^2 = f_{rr}/2\hbar c^2. \quad (40) $$

It is now easy to see that the harmonic oscillator normal mode basis functions are eigenfunctions of $H^0$. $H'_2$ gives rise to the diagonal matrix element $\lambda(v_1 - v_3)$ in equation (25), and has no off-diagonal elements within a single $v$ block. $H'_2$ does have small off-diagonal matrix elements connecting different values of $v$, which we are neglecting. It may seem that we should have used two different scaling factors $\alpha_1$ and $\alpha_3$ to define the coordinates $q_1$ and $q_3$, given by equation (13), with $\omega = \omega_1$ and $\omega_3$ respectively. However, in our zero order model $\omega_1 = \omega_3 = \omega_m$ as may be seen from equation (36). This allows us to use a single $\alpha$ defined by equation (13) with $\omega = \omega_m$, for both normal modes.

$H'_1$ has matrix elements off-diagonal in $v$ due to the cubic terms, satisfying $\Delta v_1 = \pm 1, \pm 3$ with $\Delta v_3 = 0$, and $\Delta v_1 = \pm 1$ with $\Delta v_3 = 0, \pm 2$. Once again these are treated by perturbation theory in a manner analogous to that described in the last section for a single oscillator, to obtain an effective hamiltonian matrix diagonal in $v$. There are also matrix elements off-diagonal in $v$ due to the quartic terms, but these are neglected: we systematically use second order perturbation theory for the cubic terms and first order for the quartic terms. This leads to the
standard expressions for terms quadratic in the vibrational quantum numbers. $x_{11}$, $x_{13}$, and $x_{33}$ make contributions to the diagonal matrix elements, and the Darling-Dennison term $K_{1133}$ contributes off-diagonal matrix elements according to the selection rule $\Delta v_1 = \pm 2$, $\Delta v_3 = \mp 2$. The general formulae for the $x_{rs}$ terms are given in Mills’ review [7], and the general formula for $K_{1133}$ is given in the appendix. When the general expressions for $x_{11}$, $x_{13}$, $x_{33}$, and $K_{1133}$ are specialized to the problem considered here, in which the only cubic and quartic anharmonic terms are those in (39) and (40) derived from the morse anharmonicity in the bond stretches, we obtain

$$
x_{11}(\text{morse}) = x_{33}(\text{morse}) = \phi_{1111}/16 - 5\phi_{1111}/48\omega_m,
$$

$$
x_{13}(\text{morse}) = K_{1133}(\text{morse}) = \phi_{1111}/4 - 5\phi_{1111}/12\omega_m.
$$

Using equations (39) and (40), and the formulae for a diatomic morse oscillator given in §2, we arrive at the relations (24), and the matrix elements summarized in (25) and (26).

Finally we comment on the small constant difference of $x_m/4$ between the energy levels calculated from this model in the local mode and normal mode representations. This arises from small contributions to the zero point energy from the perturbation treatment of the cubic and quartic anharmonic terms, which are customarily neglected (as we have done in the above equations) because they are generally not experimentally observable. If they were included they would add the quantity $(\phi_4/16) - (7\phi_3^3/576\omega)$ to all term values of a diatomic oscillator (this is the term $Y_{00}$ in the Dunham expansion, see for example Herzberg: Spectra of diatomic Molecules [8], p. 109). For a morse oscillator these terms exactly cancel when $\phi_3$, $\phi_4$ and $\omega$ are related back to the morse parameters, so that there is no zero point energy correction to equations (16) or (18). However the analogous corrections in the perturbation treatment leading to equation (25) do not cancel; when these are included they lead to an extra term $x_m/4$, which exactly removes the discrepancy between the two representations.

4. THREE EQUIVALENT BOND OSCILLATORS: NH$_3$

Once again we ignore all but the three XH stretching vibrations. We consider two effective vibrational hamiltonian matrices which we shall show to be equivalent, the one expressed in terms of local mode basis functions and the other in terms of normal mode basis functions.

(i) The local mode basis

We set up local mode basis functions which we denote $|l, m, n\rangle$, where the three indices represent the number of quanta of excitation in the three independent bond stretching coordinates $r_a$, $r_b$ and $r_c$ respectively. For a total vibrational excitation of $v$ quanta, where $v = l + m + n$, the number of basis functions is given by the number of ways of distributing $v$ quanta among the three bonds, which is $\binom{v+2}{v} = (v+2)!/v!2!$; thus for example the number of basis functions is 3, 6, 10 and 16 for $v = 1, 2, 3$ and 4 respectively. We take the hamiltonian
Normal modes and local modes

matrix to be factorized into blocks of this size, ignoring matrix elements that are off-diagonal in \( v \). The matrix elements within each \( v \) block are given by

\[
\langle l, m, n|H/hc|l, m, n\rangle = \omega_m(l + m + n + 3/2) + x_m[(l + \frac{1}{2})^2 + (m + \frac{1}{2})^2 + (n + \frac{1}{2})^2], \tag{43}
\]

\[
\langle l + 1, m - 1, n|H/hc|l, m, n\rangle = \lambda[(l + 1)m]^{1/2}, \tag{44}
\]

The physical significance of the parameters \( \omega_m, x_m \) and \( \lambda \) is entirely similar to that for XH\(_2\) molecules: \( \omega_m \) and \( x_m \) define the morse potential for each bond through equations (1), (4) and (5), and \( \lambda \) is related to the kinetic and potential coupling terms between each pair of bonds through equation (20). We are assuming that the off-diagonal \( g \) and \( f \) matrix elements, \( g_{rr'} \) and \( f_{rr'} \), are the same for each pair of XH bonds (as would be true by symmetry in molecules with a three-fold axis).

If \( \lambda = 0 \) we obtain the pure local mode limit, and the energy levels are given by the diagonal matrix elements in (43). The lowest lying energy levels for a given value of \( v \) are then those in which the vibrational excitation is concentrated into a single bond, and the highest lying levels are those for which the vibrational excitation is evenly disposed between the bonds.

(ii) The normal mode basis

The normal mode basis functions are denoted \( \{|v_1, v_3, l_3\rangle \} \), where \( v_1 \) and \( v_3 \) are the number of quanta in the symmetric and the doubly degenerate XH\(_3\) stretching vibrations \( v_1 \) and \( v_3 \), of symmetry species \( A_1 \) and \( E \) respectively in \( C_{3v} \), and \( l_3 \) is the angular momentum quantum number associated with \( v_3 \). The matrix is assumed to be block diagonal in \( v = v_1 + v_3 \). The matrix elements within each \( v \) block are taken to be

\[
\langle v_1, v_3, l_3|H/hc|v_1, v_3, l_3\rangle = \omega_1(v_1 + \frac{1}{2}) + \omega_3(v_3 + 1) + x_{11}(v_1 + \frac{1}{2})^2 + x_{33}(v_3 + 1)^2 + x_{13}(v_1 + \frac{1}{2})(v_3 + 1) + g_{33}l_3^2, \tag{45}
\]

\[
\langle v_1 + 2, v_3 - 2, l_3|H/hc|v_1, v_3, l_3\rangle = (1/4)K_{1133}[(v_1 + 1) \\
\times (v_1 + 2)(v_3 - l_3)(v_3 + l_3)]^{1/2}, \tag{46}
\]

\[
\langle v_1 + 1, v_3 - 1, l_3 \pm 3|H/hc|v_1, v_3, l_3\rangle = (3/8)K_{1333}[(v_1 + 1)(v_3 \pm l_3 + 2)(v_3 \mp l_3 - 2)(v_3 \mp l_3)]^{1/2}. \tag{47}
\]

(The other off-diagonal matrix elements may be determined by hermitian conjugation from those given above.) The off-diagonal matrix elements in equations (46) and (47) define the two kinds of Darling–Dennison resonance interaction that may occur between overtone levels of \( v_1 \) and \( v_3 \), which have not been previously discussed (so far as we are aware). They satisfy the selection rule \( \Delta v_1 = \pm 2, \Delta v_3 = \mp 2, \Delta l_3 = 0 \) for which the matrix elements are defined in (46) and for which we denote the coefficient \( K_{1133} \); and \( \Delta v_1 = +1, \Delta v_3 = -1, \Delta l_3 = \pm 3, \) or \( \Delta v_1 = -1, \Delta v_3 = +1, \Delta l_3 = \pm 3 \) for which the matrix elements are defined in (47) and for which we denote the coefficient \( K_{1333} \). Just as in H\(_2\)O where \( K_{1133} \) causes resonance between the upper states of \( 2v_1 \) and \( 2v_3 \), in NH\(_3\) \( K_{1333} \) couples
the upper states of $2v_1(A_1)$ and $2v_3^0(A_2)$, whereas $K_{1333}$ couples the upper states of $v_1 + v_3^1(E)$ and $2v_3^2(E)$. These new types of Darling–Dennison resonance are discussed further in the appendix, where we also derive the general formulae for the coefficients.

Finally we impose the following relations between the parameters in (45), (46) and (47).

\[
\begin{align*}
\omega_1 &= \omega_m + 2\lambda, \quad \omega_3 = \omega_m - \lambda, \quad (48) \\
x_{11} &= (2/3)x_{33} = (1/4)x_{13} = -2g_{33} = (1/3)x_m, \quad (49) \\
K_{1133} &= (3/\sqrt{2})K_{1333} = (4/3)x_m. \quad (50)
\end{align*}
\]

The physical significance of the parameters $\omega_m$, $x_m$ and $\lambda$ remains exactly as before, and the origin of the relations (48), (49) and (50) is discussed below. The matrix elements may thus be rewritten in the form

\[
\begin{align*}
\langle v_1, v_3 | H/\hbar c | v_1, v_3 \rangle &= \omega_m(v_1 + v_3 + 3/2) + \lambda(2v_1 - v_3) \\
&\quad + (1/6)x_m[2(v_1 + \frac{1}{2})^2 + 3(v_3 + 1)^2] \\
&\quad + 8(v_1 + \frac{1}{2})(v_3 + 1) - l_3^2], \quad (51)
\end{align*}
\]

\[
\begin{align*}
\langle v_1 + 1, v_3 - 2, l_3 | H/\hbar c | v_1, v_3, l_3 \rangle \\
&= (1/3)x_m[(v_1 + 1)(v_1 + 2)(v_3 - l_3)(v_3 + l_3)]^{1/2}, \quad (52)
\end{align*}
\]

\[
\begin{align*}
\langle v_1 + 1, v_3 - 1, l_3 + 3 | H/\hbar c | v_1, v_3, l_3 \rangle \\
&= (\sqrt{2/6})x_m[(v_1 + 1)(v_3 + l_3 + 2)(v_3 + l_3 - 2)(v_3 + l_3)]^{1/2}. \quad (53)
\end{align*}
\]

(iii) The Hamiltonian Operator

Once again we find that the effective vibrational hamiltonian in the normal mode basis defined in equations (51) to (53) has the same eigenvalues as the matrix in the local mode basis defined in (43) and (44), except for a change in the energy zero: the term values in the normal mode basis are all larger than those in the local mode basis by $x_m/2$. The apparently different matrices represent the same hamiltonian in two different sets of basis functions, as we now show.

The hamiltonian operator from which the above matrices may be derived may be written as the sum of three terms, in a manner exactly analogous to the hamiltonian for $XH_2$ molecules discussed previously. We write $H = H^0 + H'_1 + H'_2$, where

\[
\begin{align*}
H^0 &= \frac{1}{2}g_{rr}(\hat{\beta}_r^2 + \hat{\beta}_b^2 + \hat{\beta}_c^2) + \frac{1}{2}f_r(r_a^2 + r_b^2 + r_c^2), \quad (54) \\
H'_1 &= -\frac{1}{2}f_r(r_a^2 + r_b^2 + r_c^2) + V_m(r_a) + V_m(r_b) + V_m(r_c), \quad (55) \\
H'_2 &= g_{rr}(\hat{\beta}_r \hat{\beta}_b + \hat{\beta}_r \hat{\beta}_c + \hat{\beta}_b \hat{\beta}_c) + f_r(r_a r_b + r_b r_c + r_c r_a). \quad (56)
\end{align*}
\]

The local mode basis functions $|l, m, n\rangle$ are eigenfunctions of $H^0$. $H'_1$ has only diagonal matrix elements within a given $v$ block, and the matrix elements of $H^0 + H'_1$ together give rise to the diagonal matrix elements in equation (43). By
transforming to dimensionless coordinates \( a, b, c \) and their corresponding momenta \( \dot{a}, \dot{b}, \dot{c} \) we find that \( \mathcal{H}'_2 \) may be written in the form

\[
\mathcal{H}'_2 = \hbar \omega_m [(g_{rr}/g_{mn})(\dot{a} \dot{r} + \dot{b} \dot{b} + \dot{c} \dot{c}) + (f_{rr}/f_{mn})(a b_c + b q_c + c q_a + a q_a)].
\]  

(57)

It is then easy to see that \( \mathcal{H}'_2 \) gives rise to the matrix elements in (44). Thus (43) and (44) together give the matrix of the Hamiltonian in the local mode basis.

To find the matrix elements of the Hamiltonian in normal mode basis functions, we first transform to symmetry coordinates \( S_1, S_3, S_3x, S_3y \), and then to the corresponding dimensionless normal coordinates \( q_1, q_3, q_3x, q_3y \), defined by

\[
\begin{align*}
S_1 &= (r_a + r_b + r_c)/\sqrt{3}, & q_1 &= \alpha^{1/2}S_1, \\
S_3x &= (2r_a - r_b - r_c)/\sqrt{6}, & q_{3x} &= \alpha^{1/2}S_{3x}, \\
S_3y &= (r_b - r_c)/\sqrt{2}, & q_{3y} &= \alpha^{1/2}S_{3y},
\end{align*}
\]  

(58)

where \( \alpha \) is given in (13). The result is:

\[
\begin{align*}
\mathcal{H}_0/\hbar c &= \frac{1}{2} \omega_m (\dot{q}_1^2 + \dot{q}_2^2) + \frac{1}{2} \omega_m (\dot{q}_{3x}^2 + \dot{q}_{3y}^2), \\
\mathcal{H}'_1/\hbar c &= \frac{1}{12} \phi_{333} q_1^2 + \frac{1}{4} \phi_{333} q_1 (q_{3x} + q_{3y}) \\
&+ (1/24) \phi_{133} q_1^4 + (1/4) \phi_{133} q_1^2 (q_{3x}^2 + q_{3y}^2) \\
&+ (1/24) \phi_{333} q_1^2 (q_{3x}^2 + q_{3y}^2 + q_3^4) \\
&+ (1/6) \phi_{133} q_1 (q_{3x}^3 - 3q_{3x} q_{3y}^2), \\
\mathcal{H}'_2/\hbar c &= \frac{1}{3} \omega_m [(g_{rr}/g_{mn})(2\dot{q}_1^2 - \dot{q}_{3x}^2 - \dot{q}_{3y}^2) \\
&+ (f_{rr}/f_{mn})(2q_1^2 - q_{3x}^2 - q_{3y}^2)].
\end{align*}
\]  

(59, 60, 61)

In these equations the cubic and quartic \( \phi \) constants are related to the corresponding Morse constants by

\[
\begin{align*}
\phi_{111} &= \phi_{133} = \sqrt{2} \phi_{333} \\
&= F_{111}/\hbar c \alpha^{3/2} = f_{rrr}/\sqrt{3} \hbar c \alpha^{3/2}, \\
\phi_{1111} &= \phi_{1133} = (2/3) \phi_{3333} = \sqrt{2} \phi_{1333}, \\
&= F_{1111}/\hbar c^2 = f_{rrr}/3 \hbar c^2.
\end{align*}
\]  

(62, 63)

We can now see that \( \mathcal{H}_0 + \mathcal{H}'_2 \) give rise to the first two terms, involving \( \omega_m \) and \( \alpha \), in (51). The cubic and quartic terms in \( \mathcal{H}'_1 \) are treated by perturbation theory to give a matrix block diagonal in \( \nu \); the perturbation treatment introduces the anharmonic constants \( x_{11} \), \( x_{13} \), \( x_{33} \), and \( x_{333} \), which make contributions to the diagonal matrix elements in (45), and the Darling–Dennison constants \( K_{1133} \) and \( K_{1333} \) which give rise to the off-diagonal matrix elements (46) and (47). The general formulae for the \( x \) and \( g \) constants are given in reference [7], and the formulae for the two Darling–Dennison constants are given in the appendix. When these general formulae are specialized by omitting all contributions except those derived from the Morse anharmonicity of the bond stretching coordinates, given in equations (62) through (65) above, and when the constants \( f_{rr} \) and \( f_{rr} \) are related to the Morse diatomic parameters as in §2, then we arrive at the relations (48) through (50), and hence at the formulae for the matrix elements.
given in (51), (52) and (53). The difference of $x_m/2$ in the energy zero obtained from the two matrices arises from the neglect of small cubic and quartic anharmonic contributions to the zero point energy, as was the case for the two-bond oscillator example described in § 3.

5. FOUR EQUIVALENT BOND OSCILLATORS: CH$_4$

(i) The local mode basis

We adopt local mode basis functions $|k, l, m, n\rangle$, where the indices represent the number of quanta of excitation in $r_a$, $r_b$, $r_c$ and $r_d$ respectively. For $v = k + l + m + n$ quanta there are $\binom{v+3}{v} = (v+3)!/v!3!$ basis functions. We take the matrix to be block diagonal in $v$, with matrix elements in the local mode basis given by

\[
\langle k+1, l-1, m, n|H/hc|k, l, m, n\rangle = \lambda[(k+1)!]^{1/2}, \quad \text{etc.} \tag{65}
\]

The parameters $\omega_m$ and $x_m$ relate to the Morse function for each independent bond oscillator (equations (1), (4) and (5)), and $\lambda$ relates to the kinetic and potential coupling terms between each pair of bonds (equation (20)); $\lambda = 0$ would give the pure local mode limit, in which the energy levels are given by the diagonal matrix elements given in (64).

(ii) The normal mode basis

The H-stretching normal vibrations of CH$_4$ are $v_1$ ($A_1$) and $v_3$ ($F_2$). Because of the three-fold degeneracy of the latter the normal mode basis functions for $v_3$ may be chosen in several different ways. The choice most readily adapted to spherical tensor techniques is the set of functions denoted $|v_3, l_3, k_{13}\rangle$ by Hougen [9], where $v_3$ is the total excitation in $v_3$, $l_3$ is the total vibrational angular momentum quantum number, and $k_{13}$ is its molecule-fixed component. However for our present purposes it is somewhat easier to use cartesian components of the triply degenerate coordinates, and to adopt the corresponding basis functions denoted $|v_{3x}, v_{3y}, v_{3z}\rangle$, which are products of harmonic oscillator functions in the coordinates $q_{3x}, q_{3y}$ and $q_{3z}$. Thus when the $v_1$ basis function is included we obtain the normal mode basis functions which we shall denote $|v_1, v_{3x}, v_{3y}, v_{3z}\rangle$, where the total H stretching excitation is given by $v = v_1 + v_3 = v_1 + v_{3x} + v_{3y} + v_{3z}$. The matrix elements in this basis are given by the following expressions.

\[
\langle v_1, v_{3x}, v_{3y}, v_{3z}|H/hc|v_1, v_{3x}, v_{3y}, v_{3z}\rangle = \omega_1(v_1 + \frac{1}{2}) + \omega_3(v_3 + 3/2) + x_{11}(v_1 + \frac{1}{2})^2
\]
\[
+ x_{13}(v_1 + \frac{1}{2})(v_3 + 3/2) + x_{33}(v_3 + 3/2)^2
\]
\[
+ 2(G_{33} + 2T_{33})(v_3 + v_{3y}v_{3z} + v_{3z}v_{3x} + v_{3x}v_{3y})
\]
\[
+ T_{33}[4(v_{3x}^2 + v_{3y}^2 + v_{3z}^2)
\]
\[
- 12(v_3v_{3y}v_{3z} + v_{3z}v_{3x} + v_{3x}v_{3y}) - 8v_3], \tag{66}
\]
Normal modes and local modes

\[ \langle v_1, v_{3x}, v_{3y}, v_{3z} - 2 | H/\hbar | v_1, v_{3x}, v_{3y}, v_{3z} \rangle \]

\[ = - (G_{33} + 2T_{33}) [(v_{3y} + 1)(v_{3y} + 2)v_{3z}(v_{3z} - 1)]^{1/2}, \] (67)

\[ \langle v_1 + 2, v_{3x} - 2, v_{3y}, v_{3z} | H/\hbar | v_1, v_{3x}, v_{3y}, v_{3z} \rangle \]

\[ = (K_{1133}/4) [(v_1 + 1)(v_1 + 2)v_{3x}(v_{3x} - 1)]^{1/2}, \] (68)

\[ \langle v_1 + 1, v_{3x} + 1, v_{3y} - 1, v_{3z} - 1 | H/\hbar | v_1, v_{3x}, v_{3y}, v_{3z} \rangle \]

\[ = (K_{1333}/4) [(v_1 + 1)v_{3x} + 1] v_{3y} v_{3z}]^{1/2}. \] (69)

(Other non-zero off diagonal matrix elements are as implied by permutation of \( x, y, z \), and by hermitian conjugation, from the formulae given above.) The matrix elements in (66) and (67) include terms with coefficients \( G_{33} \) and \( T_{33} \), as defined by Hecht [10] (see also Gray and Robiette [11]). The combination \( G_{33} + 2T_{33} \) appears as the coefficient of the vibrational angular momentum operator \( l_i \), which would be diagonal with the matrix element \( l_3(l_3 + 1) \) in the \( |v_1, v_3, l_3, \ell_3 \rangle \) basis functions.

The off-diagonal matrix elements (68) and (69) define the two kinds of Darling–Dennison resonance which may occur between the overtones of \( v_1 \) and \( v_3 \). Thus \( K_{1133} \) couples together the upper states of \( 2v_1 \) and \( 2v_3 \) \( (A_1) \), and \( K_{1333} \) couples the upper states of \( v_1 + v_3 \) and \( 2v_3 \) \( (F_2) \). These resonances are discussed further in the appendix, where we also present general formulae for the coefficients \( K_{1133} \) and \( K_{1333} \) in terms of the cubic and quartic anharmonic force constants. The corresponding formulae for the other anharmonic constants, \( x_{11}, x_{13}, x_{33}, G_{33} \) and \( T_{33} \), are all given by Hecht [9]. (In passing, we note that the off-diagonal matrix element in (67) might be thought of as a kind of Darling–Dennison resonance between the overtones of different components of the vibration \( v_3 \).)

The local mode model is obtained by imposing the following relations between the parameters in equations (66) through (69), as discussed further below.

\[ \omega_1 = \omega_m + 3\lambda, \quad \omega_3 = \omega_m - \lambda, \] (70)

\[ x_{11} = (1/4)x_{13} = (5/9)x_{33} = (1/4)x_m, \] (71)

\[ G_{33} = 3T_{33} = -(3/20)x_m, \] (72)

\[ K_{1133} = (1/4)K_{1333} = x_m. \] (73)

Thus once again all the matrix elements may be expressed in terms of the parameters \( \omega_m, x_m, \) and \( \lambda \), where \( \omega_m \) and \( x_m \) characterize the morse function of each of the four equivalent bond oscillators, and \( \lambda \) characterizes the kinetic and potential coupling between each pair of bond oscillators. The final formulae for the matrix elements are as follows.

\[ \langle v_1, v_{3x}, v_{3y}, v_{3z} | H/\hbar | v_1, v_{3x}, v_{3y}, v_{3z} \rangle \]

\[ = \omega_m(v_1 + v_3 + 2) + \lambda(3v_1 - v_3) \]

\[ + (1/4)x_m[(v_1 + \frac{1}{2})^2 + 4(v_1 + \frac{1}{2})(v_3 + 3/2) + v_3^2 + 5v_3 \]

\[ + 2(v_{3y}v_{3z} + v_{3z}v_{3x} + v_{3x}v_{3y}) + (81/20)], \] (74)

\[ \langle v_1, v_{3x}, v_{3y} + 2, v_{3z} - 2 | H/\hbar | v_1, v_{3x}, v_{3y}, v_{3z} \rangle \]

\[ = (1/4)x_m[(v_{3y} + 1)(v_{3y} + 2)v_{3z}(v_{3z} - 1)]^{1/2} \] (75)
\[
\langle v_1 + 2, v_{3x} - 2, v_{3y}, v_{3z} | H/\hbar c | v_1, v_{3x}, v_{3y}, v_{3z} \rangle = (1/4)x_m[(v_1 + 1)(v_1 + 2)v_{3x}(v_{3x} - 1)]^{1/2},
\]
\[
\langle v_1 + 1, v_{3x} + 1, v_{3y} - 1, v_{3z} - 1 | H/\hbar c | v_1, v_{3x}, v_{3y}, v_{3z} \rangle = x_m[(v_1 + 1)(v_{3x} + 1)v_{3y}v_{3z}]^{1/2}.
\]

(iii) The Hamiltonian operator

As in the previous example, we find that the Hamiltonian in the normal mode representation (74)–(77) gives the same eigenvalues as the Hamiltonian in the local mode representation (64) and (65), except for a small change in the energy zero. The Hamiltonian operator involved in either case may be written as the sum of the usual three terms: \( H = H^0 + H'_1 + H'_2 \), where \( H^0 \) represents four independent harmonic bond oscillators, \( H'_1 \) represents anharmonic corrections to the potential energy terms in \( H^0 \) that transform the harmonic oscillators to morse oscillators, and \( H'_2 \) represents kinetic and potential interaction terms between the pairs of oscillators.

\[
H^0 = \frac{1}{2}g_{rr}(\hat{p}_{ra}^2 + \hat{p}_{rb}^2 + \hat{p}_{rc}^2 + \hat{p}_{rd}^2) + \frac{1}{2}f_{rr}^2 + f_{rb}^2 + f_{rc}^2 + f_{rd}^2,
\]
\[
H'_1 = -\frac{1}{2}f_{rr}(r_a^2 + r_b^2 + r_c^2 + r_d^2) + V_m(r_a) + V_m(r_b) + V_m(r_c) + V_m(r_d),
\]
\[
H'_2 = g_{rr}(\hat{p}_{ra}\hat{p}_{rb} + \hat{p}_{ra}\hat{p}_{rc} + \hat{p}_{ra}\hat{p}_{rd} + \hat{p}_{rb}\hat{p}_{rc} + \hat{p}_{rb}\hat{p}_{rd} + \hat{p}_{rc}\hat{p}_{rd})
\]
\[
+ f_{rr}(r_a r_b + r_a r_c + r_a r_d + r_b r_c + r_b r_d + r_c r_d).
\]

The way in which this Hamiltonian gives rise to the matrices presented above follows in a manner analogous to that described in the previous sections. Only the development in the normal mode basis deserves a few further comments. We adopt symmetry combinations \( (S_1, S_{3x}, S_{3y}, S_{3z}) \) of the four bond stretching coordinates \( (r_a, r_b, r_c, r_d) \) as specified by Gray and Robiette [11] in table 1 of their paper. This leads to relations between the cubic and quartic force constants in symmetry coordinates \( (F_{ijk}, F_{ijkl}) \) and the morse bond stretching coordinates \( (f_{rr}, f_{rr}) \) as specified in their table 2. We define the dimensionless normal coordinates by the usual relations

\[
q_1 = \alpha^{1/2}S_1, \quad q_{3x} = \alpha^{1/2}S_{3x}, \quad \text{etc.},
\]

where \( \alpha \) is given in equation (13). The corresponding force constants \( \phi_{rst} \) and \( \phi_{rstu} \) may then be related to the morse bond stretching force constants, giving

\[
\phi_{111} = \phi_{133} = \phi_{333} = f_{rr}/2\hbar c \alpha^{3/2},
\]
\[
\phi_{1111} = \phi_{1133x} = \phi_{33x3x3x} = \phi_{13x3y3z} = f_{rr}/4\hbar c \alpha^2.
\]

Finally, we take the general expressions for the anharmonic constants \( x_{11}, x_{13}, x_{33}, G_{33} \) and \( T_{33} \) given by Hecht [9], and for the Darling–Dennison constants \( K_{1133} \) and \( K_{1333} \) given in the appendix, and we retain only those terms arising from morse anharmonicity in the bond stretches as specified above. This leads to the relations

\[
x_{11} = x_{13}/4 = (5/9)x_{33} = -(5/3)G_{33} = -5T_{33}
\]
\[
= K_{1133}/4 = K_{1333}/16
\]
\[
= (1/16)\phi_{1111} - (5/48)\phi_{1111}/\omega_m.
\]
By using equations (82) and (83), and the appropriate relations for the diatomic morse oscillator given earlier, we then arrive at the relations (71), (72) and (73). In deriving these relations it is helpful to note that the quartic anharmonic constants \( c_{rst} \) and \( d_{stu} \) defined by Hecht [9] are related to the more general notation of Hoy et al. [5] adopted here by the equations

\[
\begin{align*}
\phi_{1111}/6, & \quad \phi_{1133}/2, & \quad \phi_{3333}, \\
\phi_{1111}/24, & \quad \phi_{1133}/4, \\
d_{3333} + d_{3333} & \quad = \phi_{3x3x3x3x}/24, \\
2d_{3333} - 3d_{3333} & \quad = \phi_{3x3x3y3y}/4.
\end{align*}
\]

The small discrepancy in the energy zero between the hamiltonians in the local mode and normal mode representations arises from the neglect of small contributions to the zero point energy from the perturbation treatment of the cubic and quartic anharmonicity.

### 6. Discussion

The model we have used in this paper is, in the local mode basis, the same as that described by Child and Lawton [12] for the two bond case. In that sense it is not original. Child and Halonen [1] (and other authors) have given the hamiltonian matrices explicitly for low values of \( v \) in this basis, although the form of their matrices differs superficially from ours because they use symmetrized combinations of local mode basis functions. Child and Halonen also present the symmetry factorized matrices for molecular models of the NH\(_3\), CH\(_4\) and SF\(_6\) types in the local mode basis. The question of symmetry factorization is discussed further below.

The point of this paper, however, is primarily to draw attention to the fact that the model can be presented in either the local mode or the normal mode basis, with identical results. Thus we have a route by which the well established theory of vibration rotation spectroscopy built upon normal mode harmonic oscillator basis functions may be connected to the current models of local mode behaviour. Almost all publications on local mode theory so far have been formulated only in terms of local mode basis functions, which look quite different to the customary theory of vibrational spectroscopy.

We believe that this relationship may prove particularly valuable in developing a general theory for the effect of local mode behaviour on rotational structure.

This paper also draws attention to the general importance of Darling–Dennison resonance interactions. Apart from bent XH\(_2\) molecules, such as H\(_2\)O and H\(_2\)S, for which the Darling–Dennison term was originally introduced [3], this type of resonance interaction appears only to have been proposed for the CH and CD stretching overtones of C\(_2\)H\(_2\) and C\(_2\)D\(_2\) [13–15]. A necessary consequence of our model is that these terms will exist and will be important in all molecules with symmetrically equivalent XH bonds.

A further conclusion is that there is little point in attempting to derive the familiar anharmonicity constants \( x_{rs} \), \( g_{tt} \), etc. for such molecules as NH\(_3\) and CH\(_4\) by fitting the observed band origins for overtones and combinations of the hydrogen stretching modes, unless the Darling–Dennison constants \( K_{rsu} \) (or in the
most general case $K_{rs}$) are introduced at the same time. In the limiting case represented by our model, there exist simple relations between the anharmonic constants $x$, $g$, $K$, etc. such as equations (24), (49)-(50), and (71)-(73) for $XH_2$, $XH_3$, and $XH_4$ molecules respectively. We are at present working on the derivation of similar relations for other molecular types. It is possible, and may be desirable, to constrain such relations into the parameters when fitting the origins of overtone and combination bands.

These relations are, of course, based on a series of approximations. We are suggesting that all of the anharmonic constants $x$, $g$, and $K$ for bond stretching vibrations can be regarded as arising from general contributions

$$x_{rs} = x_{rs}(\text{morse}) + x_{rs}(\text{other}), \quad (86)$$

where the first term derives from the morse anharmonicity in the bond stretching coordinates and the second term from other anharmonic effects and coriolis $\zeta^2$ terms. We are suggesting that the second term in (86) may often be neglected in comparison with the first term. The model that we have described in the preceding sections then allows all the bond stretching anharmonic constants to be related to the single parameter $x_m$ describing the morse character of the bond stretching coordinate.

The approximations of our model may seem questionable. In particular, we have obtained our hamiltonian matrix by using a basis of harmonic oscillator wavefunctions, in both the local mode and the normal mode representation. Harmonic oscillator functions are, of course, a long way from being eigenfunctions of a morse oscillator for the higher vibrational levels, and one may doubt the validity of this zero order model as a basis for perturbation theory. The cubic anharmonic off-diagonal matrix elements ($\Delta v = \pm 1$, $\pm 3$) reflect this fact. However these effects are incorporated into our model in the morse anharmonicity constant $x_m$, giving an effective hamiltonian matrix that is diagonal in $v$. We believe that this effective hamiltonian will give eigenvalues that correctly reflect the morse anharmonicity of the bond oscillators up to energies approaching dissociation, just as it does for the diatomic oscillator described in §2.

Some feel for the quality of this model may be obtained by comparing its predictions with experimental data for the molecules discussed here. Table 1 compares the anharmonic constants calculated from equation (24) for $H_2O$, $H_2S$ and $C_2H_2$ with the values derived by Benedict, Plyler and their co-workers many years ago from analysis of the band origins [14-17]. In each case $x_m$ for the $XH$ bond stretching has been chosen to give a reasonable match to the observed constants for the parent molecule. For the deuterated molecules, the values of $x_m$ were scaled down in proportion to the ratio of the reduced masses for the $XH$ and $XD$ diatomics, and a similar comparison of predicted and observed constants is made. The overall agreement is remarkable, considering the simplicity of the model. Table 2 shows predictions of the anharmonic constants of $CH_4$, $CD_4$, $NH_3$ and $ND_3$. The methane predictions, based on $x_m = -60 \text{cm}^{-1}$ for the $CH$ bond, are compared with values calculated by Gray and Robiette [11] from their anharmonic force field. The corresponding force field for ammonia [5] is of lower quality and predicts anharmonic constants which seem large in comparison with those given in table 2, which are based on a value of $x_m$ for NH midway between those for CH and OH.
Table 1. Anharmonicity constants, in cm\(^{-1}\), for H\(_2\)O, H\(_2\)S and C\(_2\)H\(_2\) and the corresponding deuterated species, calculated from the normal mode representation of the local mode model, and compared with experimental values.

<table>
<thead>
<tr>
<th>Species</th>
<th>Normal species</th>
<th>Deuterated species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc(^{\dagger})</td>
<td>Obs(^{\dagger})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>(x_{11}/cm^{-1})</td>
<td>-42.0</td>
</tr>
<tr>
<td></td>
<td>(x_{13}/cm^{-1})</td>
<td>-168.0</td>
</tr>
<tr>
<td></td>
<td>(x_{33}/cm^{-1})</td>
<td>-42.0</td>
</tr>
<tr>
<td></td>
<td>(K_{1133}/cm^{-1})</td>
<td>-168.0</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>(x_{11}/cm^{-1})</td>
<td>-24.0</td>
</tr>
<tr>
<td></td>
<td>(x_{13}/cm^{-1})</td>
<td>-96.0</td>
</tr>
<tr>
<td></td>
<td>(x_{33}/cm^{-1})</td>
<td>-24.0</td>
</tr>
<tr>
<td></td>
<td>(K_{1133}/cm^{-1})</td>
<td>-96.0</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>(x_{11}/cm^{-1})</td>
<td>-24.0</td>
</tr>
<tr>
<td></td>
<td>(x_{13}/cm^{-1})</td>
<td>-96.0</td>
</tr>
<tr>
<td></td>
<td>(x_{33}/cm^{-1})</td>
<td>-24.0</td>
</tr>
<tr>
<td></td>
<td>(K_{1133}/cm^{-1})</td>
<td>-96.0</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) From equation (24), assuming \(x_m(OH) = -84\) cm\(^{-1}\), \(x_m(SH) = -48\) cm\(^{-1}\), and \(x_m(CH) = -48\) cm\(^{-1}\) (see text).

\(^{\dagger}\) From equation (24), assuming \(x_m(OH) = -44.5\) cm\(^{-1}\), \(x_m(SH) = -24.8\) cm\(^{-1}\), and \(x_m(CH) = -25.9\) cm\(^{-1}\) (see text).

\(^{\dagger}\) Data from references [16] (H\(_2\)O, D\(_2\)O), [17] (H\(_2\)S), [14] (C\(_2\)H\(_2\)) and [15] (C\(_3\)D\(_2\)).

Where detailed anharmonic force fields are available, calculations of the Darling–Dennison constants from the full force field using the expressions given in the Appendix confirm the validity of our approximate model. For example we calculate \(K_{1133} = -153.2\) cm\(^{-1}\) for H\(_2\)O from the force field of Hoy et al. [5], and \(K_{1133} = -56.3\) cm\(^{-1}\), \(K_{1333} = -251.5\) cm\(^{-1}\) for CH\(_4\) from the force field of Gray and Robiette [11]. These compare with \(-168\) cm\(^{-1}\), \(-60\) cm\(^{-1}\), and \(-240\) cm\(^{-1}\) respectively given by the approximate model in tables 1 and 2.

A further comment concerns the use of symmetry in the basis functions. In our presentation the local mode basis functions have not been symmetrized, whereas the normal mode basis functions have—leading to a further factorization of the hamiltonian matrix and consequent simplification in numerical calculations. However this difference is not essential: the local mode basis functions can easily be formed into symmetry combinations (for example the functions \(|l, m, n\rangle = |2, 0, 0\rangle, |0, 2, 0\rangle\) and \(|0, 0, 2\rangle\) for NH\(_3\) form \(A_1\) and \(E\) species combinations). The full symmetry factorization is then achieved in either basis.

When this is done, the normal mode and the local mode basis functions for \(v = 1\) are always identical, although for all higher values of \(v\) they are of course different. ‘Near local mode behaviour’ might be described as occurring when the vibrational wavefunctions are close to the local mode basis functions, and ‘near normal mode behaviour’ when they are close to the normal mode basis functions; in this sense the question of local mode or normal mode behaviour for a particular molecule only arises for \(v = 2\) or greater. The competition between local mode and normal mode behaviour for \(v \geq 2\) depends on the relative magnitudes of \(x_m\) and \(\lambda\) in our model. There is a general tendency for the lower values of \(v\) to be closer to the normal mode limit, and the higher values to the local mode limit,
Table 2. Anharmonicity constants, in cm$^{-1}$, for CH$_4$, CD$_4$, NH$_3$ and ND$_3$ calculated from the normal mode representation of the local mode model. The values for methane are compared with values from Gray and Robiette [11].

<table>
<thead>
<tr>
<th>Species</th>
<th>Normal species</th>
<th>Deuterated species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc†</td>
<td>Calc‡</td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_{11}$/cm$^{-1}$</td>
<td>-15·0</td>
<td>-11·0</td>
</tr>
<tr>
<td>$x_{13}$/cm$^{-1}$</td>
<td>-60·0</td>
<td>-50·3</td>
</tr>
<tr>
<td>$x_{33}$/cm$^{-1}$</td>
<td>-27·0</td>
<td>-29·2</td>
</tr>
<tr>
<td>$G_{33}$/cm$^{-1}$</td>
<td>+9·0</td>
<td>+12·1</td>
</tr>
<tr>
<td>$T_{33}$/cm$^{-1}$</td>
<td>+3·0</td>
<td>+3·4</td>
</tr>
<tr>
<td>$K_{1133}$/cm$^{-1}$</td>
<td>-60·0</td>
<td></td>
</tr>
<tr>
<td>$K_{133}$/cm$^{-1}$</td>
<td>-240·0</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_{11}$/cm$^{-1}$</td>
<td>-24·0</td>
<td></td>
</tr>
<tr>
<td>$x_{13}$/cm$^{-1}$</td>
<td>-96·0</td>
<td></td>
</tr>
<tr>
<td>$x_{33}$/cm$^{-1}$</td>
<td>-36·0</td>
<td></td>
</tr>
<tr>
<td>$G_{33}$/cm$^{-1}$</td>
<td>+12·0</td>
<td></td>
</tr>
<tr>
<td>$K_{1133}$/cm$^{-1}$</td>
<td>-96·0</td>
<td></td>
</tr>
<tr>
<td>$K_{133}$/cm$^{-1}$</td>
<td>-45·3</td>
<td></td>
</tr>
</tbody>
</table>

† From equations (73–75) for CH$_4$ with $x_m = -60$ cm$^{-1}$, and from equations (49–59) for NH$_3$ with $x_m = -72$ cm$^{-1}$.
‡ From the above equations with $x_m$(CD) = -32·3 cm$^{-1}$ and $x_m$(ND) = -38·4 cm$^{-1}$.
§ Calculated from the full anharmonic force field [11].

owing to the fact that the Darling-Dennison off-diagonal terms in the normal mode basis increase as $v^2$, whereas the interbond coupling off-diagonal terms in the local mode basis only increase as $v$ to the first power. Physically this reflects the fact that Morse anharmonicity becomes more and more dominant over interbond coupling as we approach dissociation, so that local mode effects always tend to win at high vibrational energies.

I.M.M. would like to express his thanks to the Molecular Spectroscopy Section of the National Bureau of Standards, Washington, D.C., for an invitation to spend time there as a Guest Scientist, during which part of this work was completed.

APPENDIX

Darling-Dennison terms [3] are off-diagonal $H_{40}$ terms in the effective vibrational hamiltonian, where the indices $m, n$ in the notation $H_{mn}$ imply a term involving $m$ powers of vibrational operators ($\hat{p}$ or $\hat{q}$) and $n$ powers of rotational operators ($\hat{J}_x$, $\hat{J}_y$ or $\hat{J}_z$) [18]. The operators involved may be calculated by a contact transformation of the original hamiltonian, or their matrix elements may be calculated by Van Vleck perturbation theory from the general formula

$$
\langle v_i | \hat{H}_{40} | v_j \rangle = \langle v_i | H_{40} | v_j \rangle + \sum_k \frac{\langle v_i | H_{30} | v_k \rangle \langle v_k | H_{30} | v_j \rangle}{(E_{ij} - E_k)}. \tag{A1}
$$

Here $v_i$, $v_j$ and $v_k$ are collective symbols for the vibrational quantum numbers, and $v_i$ and $v_j$ denote levels that would be degenerate in the zeroth order approximation, so that $E_i \approx E_j$; $E_{ij}$ denotes the mean energy $(E_i + E_j)/2$. Thus contribu-
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tions arise from \( H_{40} \) and \( H_{30} \) terms in the untransformed hamiltonian, the former by first order perturbation theory and the latter by second order perturbation theory.

For \( \text{H}_2\text{O} \) Darling–Dennison resonance arises between pairs of states such as the upper states of the \( 2v_1 \) and \( 2v_3 \) bands. The general formula for the matrix elements is

\[
\langle v_1 + 2, v_3 | H/hc | v_1, v_3 + 2 \rangle = (1/4)K_{1133}[(v_1 + 1)(v_1 + 2)(v_3 + 1)(v_3 + 2)]^{1/2}
\]

(A 2)

Contributions arise from the following terms in the original hamiltonian:

\[
H_{40}/hc = (1/4)\phi_{1133} q_1^2 q_3^2 + C(\zeta_{13})^2
\]

\[
\times [q_1 \hat{p}_3 (\omega_3/\omega_1)^{1/2} - q_3 \hat{p}_1 (\omega_1/\omega_3)^{1/2}]
\]

(A 3)

\[
H_{30}/hc = (1/6)\phi_{111}q_1^3 + \frac{1}{2}\phi_{112} q_1^2 q_2 + \frac{1}{2}\phi_{133} q_1 q_2^2 + \frac{1}{2}\phi_{233} q_2 q_3^2.
\]

(A 4)

Application of equation (A 1) then gives the coefficient as

\[
K_{1133} = (1/4)\phi_{1133} - 4C(\zeta_{13})^2 + (1/12)\phi_{111}\phi_{133}/\omega_{13}
\]

\[
+ (1/4)\phi_{112} \phi_{233} \omega_2/(4\omega_{13} - \omega_2) - \phi_{133}^2/2\omega_{13}.
\]

(A 5)

In Darling and Dennison’s original paper [3] the coefficient is denoted \( \gamma \), where \( K_{1133} = 2\gamma \).

A similar development for \( \text{C}_2\text{H}_2 \) leads to identical formulae, provided that the \( C(\zeta_{13})^2 \) terms are deleted from equations (A 3) and (A 5).

In \( \text{NH}_3 \) two kinds of Darling–Dennison resonance occur. The general formulae for the matrix elements are

\[
\langle v_1 + 2, v_3 - 2, l_3 | H/hc | v_1, v_3, l_3 \rangle = (1/4)K_{1133}[(v_1 + 1)(v_1 + 2)(v_3 - l_3)(v_3 + l_3)]^{1/2},
\]

(A 6)

\[
\langle v_1 + 1, v_3 - 1, l_3 \pm 3 | H/hc | v_1, v_3, l_3 \rangle = (3/8)K_{1133}[(v_1 + 1)(v_3 \mp l_3 + 2)(v_3 \mp l_3 - 2)(v_3 \mp l_3)]^{1/2}.
\]

(A 7)

The contributing terms in the original hamiltonian are

\[
H_{40}/hc = (1/4)\phi_{1133} q_1^2 (q_3^2 x + q_3^2 y)
\]

\[
+ (1/6)\phi_{1333} q_1 (q_3^3 x - 3q_3 x q_3^2 y) + B(\zeta_{13})^2 (\hat{l}_x^2 + \hat{l}_y^2),
\]

(A 8)

where

\[
\hat{l}_x = [q_1 \hat{p}_3 (\omega_3/\omega_1)^{1/2} - q_3 \hat{p}_1 (\omega_1/\omega_3)^{1/2}]
\]

and

\[
\hat{l}_y = [-q_1 \hat{p}_3 (\omega_3/\omega_1)^{1/2} + q_3 \hat{p}_1 (\omega_1/\omega_3)^{1/2}],
\]

\[
H_{30}/hc = (1/6)\phi_{111}q_1^3 + \frac{1}{2}\phi_{112} q_1 q_2 + \frac{1}{2}\phi_{133} q_1 (q_3^2 x + q_3^2 y)
\]

\[
+ \frac{1}{2}\phi_{233} q_2 (q_3^2 x + q_3^2 y) + \phi_{134} q_1 (q_3 q_6 x + q_3 q_4 y) + (1/6)\phi_{333} (q_3^3 x - 3q_3 x q_3^2 y)
\]

\[
+ \frac{1}{2}\phi_{334} (q_3^2 x q_4 x - q_3^2 y q_4 y - 2q_3 x q_3 y q_4 y).
\]

(A 9)
Application of (A 1) then leads to the following formulae for the coefficients:

\[
K_{1133} = (1/4)\phi_{1133} - 4H_{11}^2
\]

\[
+ \sum_{s=1,2} (1/4)\phi_{11s}\phi_{33s}\omega_s/(4\omega_{13}^2 - \omega_s^2)
\]

\[
- \sum_{t=3,4} \phi_{13t}^2/2\omega_t,
\]

\[\text{(A 10)}\]

\[
K_{1333} = (1/6)\phi_{1333}
\]

\[
- \sum_{t=3,4} (1/6)\phi_{13t}\phi_{33t}(8\omega_{13}^2 - 3\omega_t^2)/\omega_t(4\omega_{13}^2 - \omega_t^2).
\]

\[\text{(A 11)}\]

In CH\textsubscript{4} again two kinds of Darling-Dennison resonance occur. The general formulae for the matrix elements are

\[
\langle v_1 + 2, v_{3x}, v_{3y}, v_{3z} | H/hc | v_1, v_{3x} + 2, v_{3y}, v_{3z} \rangle
\]

\[
= (1/4)K_{1133}[(v_1 + 1)(v_1 + 2)(v_{3x} + 1)(v_{3x} + 2)]^{1/2},
\]

\[\text{(A 12)}\]

\[
\langle v_1 + 1, v_{3x} + 1, v_{3y}, v_{3z} | H/hc | v_1, v_{3x}, v_{3y} + 1, v_{3z} + 1 \rangle
\]

\[
= (1/4)K_{1333}[(v_1 + 1)(v_{3x} + 1)(v_{3y} + 1)(v_{3z} + 1)]^{1/2}.
\]

\[\text{(A 13)}\]

The contributing terms in the original hamiltonian are

\[
H_{40}/hc = (1/4)\phi_{1133}\phi_{33}^2 + \phi_{1333}\phi_{41}\phi_{33}\phi_{33}
\]

where \(\phi_{33} = q_{3x}^2 + q_{3y}^2 + q_{3z}^2\), and

\[
H_{30}/hc = (1/6)\phi_{1111}q_{3x}^3 + 1/2\phi_{1333}\phi_{33}q_{33}
\]

\[
+ \phi_{1341}(q_{3x}q_{4x} + q_{3y}q_{4y} + q_{3z}q_{4z}) + \phi_{3333}(q_{3x}q_{3x}q_{3y}q_{3z})
\]

\[
+ \phi_{3334}(q_{3x}q_{3y}q_{4y}q_{3z} + q_{3x}q_{4y}q_{3y} + q_{4x}q_{3x}q_{3y}).
\]

\[\text{(A 14)}\]

Application of (A 1) then leads to the following formulae for the coefficients:

\[
K_{1133} = (1/4)\phi_{1133} + (1/12)\phi_{1111}\phi_{1333}/\omega_{13}
\]

\[
- \sum_{t=3,4} \phi_{13t}^2/2\omega_t,
\]

\[\text{(A 15)}\]

\[
K_{1333} = \phi_{1333} + \sum_{t=3,4} \phi_{13t}\phi_{33t}
\]

\[
\times (3\omega_{13}^2 - 8\omega_{13}^2)/\omega_t(4\omega_{13}^2 - \omega_t^2).
\]

\[\text{(A 16)}\]

REFERENCES

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