Local Mode Overtone Spectra

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The concept of a normal mode plays an important part in vibrational theory whether for molecules, musical instruments, or engineering structures. In molecules certain vibrational modes are localized. A familiar example is a bond vibration with a frequency so disparate from others in the molecule that it is effectively uncoupled from other degrees of freedom, such as the ν, C–H stretching mode of CHCl₃. The success of infrared spectroscopy as an analytical tool depends on recognition of characteristic local bond or local group frequencies of this type. This Account deals with a more sophisticated form of localization that can develop in molecules for which the forms of coupled normal modes are determined by symmetry. The meaning of the term “local” has subtleties attached to it in this context, but there is no doubt that the concept has had signal success in the interpretation of multiquantum (overtone) absorption spectra, which are now becoming accessible by laser spectroscopy.1,2

In order to explain this new kind of localization it is convenient to start from a classical model. Imagine a molecule containing two equivalent bonds with a common frequency ω₀. Oscillations in one of them will be resonantly excited by vibrations in the other and energy will flow between them at a frequency ω₁ governed by the strength of interbond coupling. The ensuing motion may then be decomposed into two concerted normal mode motions with frequencies ω₀ ± ω₁. This normal mode picture depends however on the harmonic approximation—Namely that ω₀ and ω₁ are independent of energy. In a more realistic anharmonic model the individual bond frequencies will vary with energy, typically decreasing, for stretching vibrations, as the energy increases. This means that highly excited bonds will have a different natural frequency ωκ from one that is unexcited. The coupling between them will therefore be effectively quenched if this anharmonic detuning is large and the interbond coupling is relatively weak. Classical studies on a realistic potential function confirm that one can observe a permanent imbalance between the two local bond excitation states of H₂O for example.3

More detailed analysis of this classical situation may be found in papers by Lawton and Child,4 Jaffe and Brumer,5 and Sibert et al.6 We note here two important observations. First, that the conditions of large anharmonicity and weak interbond coupling are most easily satisfied by the stretching of X–H bonds. Second, the two possible distributions of separate quanta in the two bonds gives rise to a twofold classical local mode degeneracy, with higher degeneracies if the number of equivalent bonds is increased.

The main purpose of this Account is to outline the quantum-mechanical analogue of this picture. One important change is that the quantum-mechanical states must of course carry the proper symmetry labels for the system. Thus the theory is developed in terms of symmetry adapted local mode states, given, in the case of two oscillations, by

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\[ |n,m^s\rangle = 2^{-1/2}(|n,m\rangle \pm |m,n\rangle) \]

where \(|n,m\rangle\) denotes a state with \(n\) local quanta in the first oscillator and \(m\) in the second. Quantum-mechanical effects also give rise to an energy splitting that lifts the strict classical degeneracy, but decreases markedly with increasing energy. Notice the analogy here between the conventional picture of atomic spectroscopy—electronic motion, of course, being far from anharmonic. The 1sns configuration of He for example corresponds to a local assignment of one electron to the 1s and the other to an ns state. The proper symmetrization gives rise to \(^{1S}\) and \(^{3S}\) terms that are split by the electrostatic interactions with a magnitude that decreases markedly with \(n\).

The strongest local mode effects in molecules are observed in the above \(|n,m^s\rangle\) states with \(n = 0\) and \(m\) increasing. These include (i) the observation that successive \(|0,m\rangle\) absorption band frequencies are well approximated by a single Morse oscillator expression, \[^{8,9}\] (ii) the development of increasingly close local mode degeneracies; \[^{10}\] (iii) predominant intensity in the \(|0,0\rangle \rightarrow |0,n\rangle\) rather than \(|0,0\rangle \rightarrow |1,n-1\rangle\) etc. absorption bands, indicative of the local excitation of a single mode; \[^{11}\] and (iv) the insensitivity of X–H bandwidths and absorption frequencies to deuteration substitution, while the intensity varies in proportion to the number of unsubstituted X–H bonds. \[^{12,13}\] It should also be noted that the widths of the bands are indicative of the rate of intramolecular transfer to the rest of the molecule. Thus the possibility of local excitation to high vibrational levels can provide a convenient means for the experimental study of this interesting process. \[^{14,15}\]

Although the most strongly developed local mode effects are seen in the \(|0,m\rangle\) excitation states, it is of interest to examine the character of other states and their energy dispositions. This not only helps complete the theoretical picture but also allows interpretation of the weaker bands in experimental overtone absorption spectra. It is here that knowledge of the relative strengths of bond anharmonicity and interbond coupling become very important. One can appreciate that strongly anharmonic and weakly coupled motions give rise to local mode effects, whereas weakly anharmonic, strongly coupled, motions are much more normal in character. These are, however, merely two extremes. There is a continuous scale between local and normal mode limits according to the ratio of bond anharmonicity to intermode coupling strength. It is shown below how one can construct a quantitative energy-level correlation diagram based on this idea, and how different molecules may be located on it. Earlier reviews of the salient features of the theory are available in the literature, \[^{8,9,11}\] as is a fuller account of the present discussion. \[^{16}\]

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**Experimental Background**

The development of local mode theory started from the observation \[^{6,8}\] that the frequencies of the strongest overtone (\(\Delta n \geq 2\)) bands are consistent with a single mode oscillator model, with Morse energy levels

\[ E_n/\hbar c = (n + \frac{1}{2})\omega - (n + \frac{1}{2})^2\omega x \quad (1) \]

If so, the \(0 \rightarrow n\) absorption frequency would become

\[ \nu_{0,n} = n\omega - (n+1)\omega x \quad (2) \]

with the prediction that \((\nu_{0,n}/n)\) should be linear in \(n\). Figure 2 shows that this is fully confirmed at high \(n\) values for a variety of molecules, the deviations for \(n\)

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**References**

Further support is provided by the variation of band intensity with isotope substitution. In benzene for example the frequencies of the dominant CH stretching overtone bands are invariant to isotopic substitution, but the integrated band intensities decrease proportionally with the number of hydrogen atoms from C\textsubscript{6}H\textsubscript{6} to C\textsubscript{6}D\textsubscript{6}.\textsuperscript{12,13} The suggestion is therefore that the local mode states of a molecule with \( N \) equivalent X–H bonds, are \( N \)-fold degenerate.

Closer analysis shows that while valid for some states this is an oversimplification. Figure 2 shows for example the observed vibrational term value for H\textsubscript{2}O\textsuperscript{10} measured in each case from the lowest term value for the appropriate manifold, the term “manifold” being used to include all stretching states with a given total quantum number. It is evident that the lowest term values do approach a well-marked local mode degeneracy as \( n \) increases, the local mode splitting for \( n = 5 \) being only 0.4 cm\textsuperscript{-1}. The approach to an equivalent sixfold degeneracy is predicted\textsuperscript{17} to be even more rapid in benzene, for which the 26 cm\textsuperscript{-1} spread of the CH stretching fundamentals\textsuperscript{18} is much smaller than the 100 cm\textsuperscript{-1} splitting in H\textsubscript{2}O. Figure 2 also shows a progressive decrease in the interval between third and fourth term values, but the general impression is one of irregularity. Thus a strict local mode description would be a gross oversimplification.

The final experimental observables to have attracted attention are the widths of different overtone peaks, and their possible relevance to the rate of intramolecular transfer from X–H modes to the rest of the molecule.\textsuperscript{18} The observations include rotationally resolvable spectra for a variety of species including H\textsubscript{2}O,\textsuperscript{10} C\textsubscript{6}H\textsubscript{6}, C\textsubscript{6}D\textsubscript{6},\textsuperscript{22-24} and SiH\textsubscript{4},\textsuperscript{25-28} with individual line widths of 0.0067 cm\textsuperscript{-1} in the case of CH\textsubscript{4}.\textsuperscript{25} On the other hand, the gas-phase spectra of larger molecules show overtone band widths of the order of 50–100 cm\textsuperscript{-1}. The most famous example is benzene for which the band widths increase from \( \sim 30 \) cm\textsuperscript{-1} at \( n = 1 \) to a maximum of \( \sim 110 \) cm\textsuperscript{-1} at \( n = 5 \) and then decrease to \( \sim 56 \) cm\textsuperscript{-1} at \( n = 9.15 \). The existence of such broad peaks is evidence that the CH mode cannot be truly local in the sense that it is decoupled from other modes in the molecule. In fact the observations in benzene have been plausibly interpreted by Sibert et al.\textsuperscript{26} in terms of a specific Fermi resonance, induced by geometrical determined momentum transfer coupling between the CH vibrations and a combination of in-plane CCH wag and C–C stretching modes. The overall band widths for both C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}D\textsubscript{6} have been shown to range from \( \sim 56 \) cm\textsuperscript{-1} to \( \sim 110 \) cm\textsuperscript{-1}, which is approximately twice the degeneracy weighted average frequency of 1283 cm\textsuperscript{-1} for the wagging and C–C stretching modes.

Coupled Local Anharmonic Oscillators

The central importance of competition between interbond coupling and bond anharmonicity may be illustrated by considering the model Hamiltonian

\[ H = \hbar \omega (n + 1/2) \omega - (n + 1/2)^3 \omega \chi I(n) \]  

In constructing the matrix of \( H \) within a local mode product basis \( |n_a n_b \rangle \) it is of vital importance to include the anharmonic term in \( \omega \chi \) eq 4, but it is sufficient for illustrative purposes to evaluate the matrix elements of \( q_a \) and \( P_a \) in the harmonic approximation; errors will be of order \( \omega \chi / \omega \). Since both \( q_a \) and \( P_a \) carry selection rules \( \Delta n_a = \pm 1 \) a given state \( |n_a n_b \rangle \) will be coupled to others such as \( |n_a \pm 1, n_b \rangle \), which differ from it in energy by terms of order \( \omega \chi \), and to other states \( |n_a + 1, n_b \rangle \) and \( |n_a - 1, n_b \rangle \) which are separated from it by energy gaps of roughly \( 2 \omega \). Since \( \omega \gg \omega \chi \) the dominant coupling will be with the former pair. Detailed analysis\textsuperscript{27-29} shows that the relevant nonzero matrix elements take the form

\[ \langle n_a + 1, n_b = 1 | H | n_a n_b \rangle = \lambda \sqrt{(n_a + 1)n_b} \]

\[ \langle n_a - 1, n_b + 1 | H | n_a n_b \rangle = \lambda \sqrt{n_a(n_b + 1)} \]

where, if second-order interactions nonresonant modes \( q_a \) with frequencies \( \omega_a \) are taken into account\textsuperscript{28}

\[ \lambda = \alpha + \beta + \sum \frac{(\alpha + \beta)^2}{\omega - \omega_a} - \frac{(\alpha - \beta)^2}{\omega + \omega_a} \]

the \( \alpha \) and \( \beta \) type terms arise from coupling via the momentum and coordinate dependent coupling, respectively. Specific expressions for these parameters are given elsewhere.\textsuperscript{26}

The coupling scheme implied by eq 4 and 5 is illustrated in Figure 3, from which it is apparent that in the case that \( \omega \chi \gg \lambda \), the lowest pair of levels for each manifold will be split in first, second, and third order for \( n_a + n_b = 1, 2, 3 \), respectively. Equally the upper level pair for \( n_a + n_b = 3 \) will be split in first order, etc. The model therefore accounts for the pattern of observed H\textsubscript{2}O term values shown in Figure 2.

Local to Normal Mode Correlations

One can proceed beyond these qualitative considerations to obtain explicit expressions for the eigenvalues.

\[ \langle n_a + 1, n_b = 1 | H | n_a n_b \rangle = \lambda \sqrt{(n_a + 1)n_b} \]

\[ \langle n_a - 1, n_b + 1 | H | n_a n_b \rangle = \lambda \sqrt{n_a(n_b + 1)} \]
respectively the variation of symmetric and antisymmetric modes, respectively. The central "local" labels, 
manifolds by means of the reduced eigenvalues

\[
\begin{array}{ccc}
0 & 3 & 3 \\
2\omega x & 2\lambda & \beta \\
0 & 2 & 1 \\
2\omega x & 2\lambda & \beta \\
0 & 4 & 2 \\
4\omega x & 2\lambda & \beta \\
\end{array}
\]

\[
\begin{array}{c}
0.1 \\
1' \text{order} \\
0.2 \\
2' \text{order} \\
0.3 \\
3' \text{order} \\
\end{array}
\]

Figure 3. The anharmonic oscillator coupling scheme: zeroth order local mode labels \([n, m]_n\) indicate individual bond excitations. \([n, n^\pm]\) are symmetrized and antisymmetrized combinations. 
Taken from Child and Halonen\(^{16}\) with permission of the publishers.

The calculation is simplified by adopting the symmetrized local mode basis with elements

\[
| n, m^\pm \rangle = 2^{-1/2}(| n, m \rangle \pm | m, n \rangle) \text{ for } n < m
\]

\[
| n, n^+ \rangle = | n, n \rangle
\]

(7)

where the first and second quantum numbers on the right-hand side refer to excitation of \(q_a\) and \(q_b\) respectively. The resulting transformed matrices are given elsewhere.\(^{28,29}\) It is convenient for presentation purposes to plot the splitting pattern for different manifolds by means of the reduced eigenvalues

\[
\epsilon = \left[ E - E(n) \right] / [\alpha^2 + (\omega x)^2]^{1/2}
\]

(8)

where \(E\) denotes the eigenvalue in question and \(E(n)\) mean eigenvalue for the manifold (i.e., the set of states with given total quantum number \((n)\). The variation of these reduced eigenvalues as a function of \((\lambda/\omega x)\) constitutes a correlation diagram between local (\(|\lambda| \ll |\omega x|\)) and normal (\(|\lambda| \gg |\omega x|\)) limits.

Its form for two coupled oscillators is shown in Figure 4. The notation adopted is that the columns labeled "normal" give the conventional normal mode specifications, with \(\nu_1\) and \(\nu_2\) as the symmetric and antisymmetric modes, respectively. The central "local" labels, \([n, m]_n\), specify the excitation states of the two local oscillators \(q_a\) and \(q_b\). Finally solid and dashed lines denote respectively the variation of symmetric and antisymmetric reduced eigenvalues, \(\epsilon\), according to the ratio \((\lambda/\omega)\). The arctan scale is adopted to cover a wide range of \((\lambda/\omega)\).

Notice that the eigenvalues are equally spaced in the limits \((\lambda/\omega x) \to \pm \infty\), in accordance with the familiar harmonic normal coordinate picture, with the ordering of levels in the odd manifolds being dependent on the sign of \((\lambda/\omega x)\). The local limit, \((\lambda/\omega x) = 0\), on the other hand gives rise to two-fold \([n, m^\pm]\) degeneracies which are split linearly, quadratically, and cubically in \((\lambda/\omega x)\) along the \([0, n^\pm]\) sequence, in accordance with the coupling scheme in Figure 3.

The vertical lines show the location of different molecules on this diagram according to the \(\lambda\) and \(\omega x\) parameters derived from their spectra;\(^{28}\) \(\omega x\) is available from the slope of \((\nu_0/n)\) vs. \((n + 1)\) as shown in Figure 1, and the fundamental splitting \((\nu_1 - \nu_2)\) may be shown to be equal to \(2\lambda\).\(^{28,29}\) Equation 6 allows us to understand the relative position of different molecules. For example the molecules in which the two modes are coupled via a central atom, give rise to negative \(\lambda\) values, this being the sign of the momentum transfer, \(\alpha\), term in eq 6, which depends on the mass ratio of the peripheral to the central atom.\(^{16}\) It is therefore not surprising that \(\text{SO}_2\) is the most normal and \(\text{H}_2\text{S}\) and \(\text{H}_2\text{Se}\) the most local of this class of molecules, and that \(\text{D}_2\text{O}\) is more normal in behavior than \(\text{H}_2\text{O}\). The potential coupling, \(\beta\), term in eq 6 are of course also relevant to the position in the diagram, and detailed analysis\(^{28}\) shows that these account in \(\text{H}_2\text{O}\) for roughly half the coupling strength \(\lambda\). The occurrence of positive \(\lambda\) values for \(\text{C}_2\text{H}_2\) and \(\text{C}_2\text{D}_2\) is also readily understood in the light of eq 6 because there is no direct momentum coupling from one CH (or CD) bond to the other and very little direct potential coupling either\(^{28,30}\) \((\beta \approx \alpha = 0)\). The dominant coupling is via the C-C mode (with coupling parameters \(\omega_a\) and \(\beta_\lambda\)) which causes a positive contribution to \(\lambda\) in eq 6 if, as is the present case, \(\omega > \omega_a\). The surprisingly large difference between near local behavior in \(\text{C}_2\text{H}_2\) and near normal behavior in \(\text{C}_2\text{D}_2\) is attributable not only to the change in mass ratio but more importantly to a much smaller resonance defect \(\omega - \omega_a\) in the deuterated than in the hydrogenated molecule.\(^{28,30}\)

Similar correlation diagrams have been worked out for \(\text{AH}_4\),\(^{22}\) \(-\text{AH}_6\),\(^{31}\) and \(\text{XY}_4\)\(^{32}\) species; the results are


Figure 4. The local to normal mode correlation diagram for two coupled oscillators, indicating the positions of various molecules. 
Taken from Child and Halonen\(^{16}\) with permission of the publishers.
collected together with the appropriate coupling matrices in a more comprehensive review elsewhere.\textsuperscript{16}

Potential Models and Variational Calculations

Early test calculations, based on a realistic but complicated potential surface for H$_2$O,\textsuperscript{30} showed that a local mode Morse oscillator basis, as defined by eq 7, gave more rapid convergence than a conventional normal mode representation.\textsuperscript{34,35} The calculated results were found to be in good agreement with experiment,\textsuperscript{14} because the potential function\textsuperscript{50} embodied a spectroscopically determined force field. One might however ask, in the light of sections 3 and 4, whether similar success could be obtained with a simpler potential function. How accurately for example could one describe the spectrum with a simple hamiltonian, as given in eq 3, if the simplifying approximations adopted in sections 3 and 4 were abandoned? The answer, for a variety of molecules, is very well indeed.

Table I gives comparisons between observed term values for CH$_4$ and SiH$_4$ and those calculated\textsuperscript{16,22} from the four-bond analogue of eq 3 with two adjustable Morse parameters, $\omega$ and $\omega x$, and one potential coupling parameter $v_{ab}$; the momentum coupling coefficient $g_{ab}$ in eq 3 depends only on masses and geometrical factors.\textsuperscript{16}

The table gives both normal mode and local mode assignments, the former for ease of comparison with the literature and the latter to emphasize the local characteristics of the situation. Notice that the observed, (presumably strongest) overtone bands are assigned in the normal mode picture to states $n\nu_1 + \nu_2$, which involve a $\Delta \nu = n$ transition in the optically inactive normal mode $\nu_1$, combined with $\Delta \nu_2 = 1$. In the local picture, on the other hand, the same transitions more plausibly involve excitation by $(n+1)$ quanta in a single bond mode.

The most striking feature of the table is however the predictive power of the three parameter model, which for CH$_4$ predicts the eight observations for $\nu = 1-3$ with a root mean square (rms) deviation of 5.4 cm$^{-1}$ and the full 20 observations with an rms deviation of 45 cm$^{-1}$. Similarly, in the case of SiH$_4$, the rms deviation from the 11 observed term values is only 8 cm$^{-1}$. Comparable results have been reported for C$_2$H$_2$ and its isotopic variants,\textsuperscript{30,36} a variety of XH$_3$D and XHD$_3$ species,\textsuperscript{32} and SF$_6$, UF$_6$, and WF$_6$.\textsuperscript{32}

The inclusion of SiH$_4$ in the table is of particular interest because the fundamental splitting $\nu_2 - \nu_1 \approx 2.32$ cm$^{-1}$. Thus SiH$_4$ is the extreme local mode molecule to have been studied in detail. SiD$_4$ on the other hand lies however roughly half way between local and normal limits in the appropriate correlation diagram.\textsuperscript{22} The reason for the difference is that the kinetic and potential contributions to the analogue of $\lambda$ in eq 6 are of equal magnitude in SiH$_4$ but have opposite signs; hence $\lambda = (\nu_2 - \nu_1)/4 \approx 0$. The kinetic (momentum transfer) term, $\alpha$, is however relatively much more important in SiD$_4$, which accounts for the difference in behavior. A similar difference occurs between GeH$_4$ and GeD$_4$,\textsuperscript{22} but the available high overtone data are relatively limited.

Relevance of the Local Mode Pictures

The previous discussion has emphasized the local mode aspects of a particular type of motion—the stretching overtones of X-H bonds. Questions now arise as to the generality of this picture.

The low mass of the H atom is peculiarly significant in this context. First it gives rise to a typical stretching frequency $\omega \sim 3000$ cm$^{-1}$ well separated from other modes, thereby minimizing coupling to other parts of the molecule, although the final part of section 2 shows that Fermi resonances may have significant effects. Secondly the anharmonicity parameter $\omega x$, which is inversely proportional to reduced mass for a Morse oscillator,\textsuperscript{57} is unusually large for XH bonds; $\omega x \sim$
50–100 cm\(^{-1}\), compared with 7.5 cm\(^{-1}\) for say SO\(_2\).\(^{26}\) Finally the inter-bond-coupling-strength term \(\lambda\) is dominated for stretching modes in most molecules, by momentum transfer terms dependent on the ratio of peripheral to central atom mass, giving rise to a value of \(\lambda \approx -100\) cm\(^{-1}\) in SO\(_2\) compared with \(\lambda \approx -50\) cm\(^{-1}\) in H\(_2\)O.\(^{28}\) The combination of the last two factors means that the ratio \([\lambda/\omega]\) is much smaller (closer to the local mode limit) in H\(_2\)O than in SO\(_2\). The arguments applying to the peculiar local mode advantages for X–H over other stretching modes apply even more strongly to bending and twisting modes which are if anything more harmonic than non X–H stretches.

One can also enquire into the effect of exciting other modes on the behavior of the X–H stretches. The experimental evidence in H\(_2\)O\(^{28}\) and theoretical evidence of C\(_2\)H\(_2\) and C\(_2\)D\(_2\)\(^{30}\) is that such excitation has remarkably little effect on the spectrum, as shown for example by minimal changes in the local mode doublet splittings when H\(_2\)O is excited to the \(v_3 = 1\) and \(v_2 = 2\) levels of its bending vibration.\(^{28}\) Thus, while local mode behavior is probably a specifically X–H stretching phenomenon, it is also a persistent one. Moreover these are the motions whose overtone states are most readily accessible by modern techniques,\(^{12,12,13}\) because one requires only 5–6 quanta of the high X–H stretching frequency to reach the convenient tunable dye laser spectroscopic region. It is therefore a happy coincidence that the new theory has been developed for the very molecules most open to experimental investigation.

**Concluding Remarks**

Attention has been concentrated above on the use of local modes for spectroscopic assignment and interpretation—an essential first step towards understanding the nature of vibrationally excited molecular motions.

The kinetic implication of local mode states have also attracted widespread attention under the heading “intra-molecular relaxation”.\(^{38}\) One knows that current theories of unimolecular dissociation assume free energy flow within the molecule,\(^{39}\) on a picosecond time scale, as required for consistency with experimental results.\(^{40}\) At very low energies on the other hand energy is locked into one particular normal or local mode; otherwise the use of quantum mechanical labels would be meaningless. At what energy and by what mechanism does the transition from low energy “regularity” to high energy “chaos” occur?

Classical studies have charted the relative phase space fractions occupied by normal, local, and chaotic states as a function of energy for simple systems.\(^{5,41,42}\) The results for the stretching states for H\(_2\)O\(^{5,41}\) suggest a significant onset of chaotic trajectories at the expense of local ones at roughly 30,000 cm\(^{-1}\), well above the highest analyzed spectroscopic bands. The regularity of the known spectrum of H\(_2\)O is consistent with this theoretical prediction.

The situation is rather different for larger molecules, with much higher densities of states. Here the existence of a significantly localized mode which is optically coupled to the ground state provides a window for observation of the strength of coupling to other degrees of freedom. The width of the band is of particular significance in giving, via the uncertainty principle \(\Delta E \Delta t \approx h\), a measure of the time \(\Delta t\) for intramolecular relaxation, if for example the band were coherently excited by a pulse short compared with \(\Delta t\).\(^{18}\) It still remains to be established however whether all or merely some other modes are excited by the relaxation. The Fermi-resonance theory cited above for the bandwidths in benzene\(^{30}\) would require relaxation only into the C–C stretching and C–H wagging degrees of freedom for example.

These are only a few of the interesting problems for future investigation. Many fascinating questions remain to be answered.


