

One-dimensional Potential Energy Functions in Vibrational Spectroscopy

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1 Introduction

Each molecule possesses $3N - 6$ fundamental vibrations ($3N - 5$ for linear molecules) where N is the number of atoms per molecule. Thus, the diatomic molecule is the only type of molecule which has only one vibration. It is sometimes assumed that this is the only situation where a one-dimensional vibrational potential function is applicable, but this is not the case. Altogether there are four types of vibrations that can be treated as one-dimensional systems. These are: the vibrations of diatomic molecules; symmetry isolated vibrations; vibrations isolated by use of a high-frequency separation; and vibrations isolated by a low-frequency separation. The last two types of vibrations are only approximately one-dimensional but can be treated as such with very little error. The low-frequency separation has been of special interest recently as it has been used to gather a considerable amount of data on molecular structures and intramolecular forces.

2 Diatomic Molecules

A. The Harmonic Oscillator.—As a first approximation, the vibration in a diatomic molecule has traditionally been envisaged as a harmonic oscillation.¹ The bond in the molecule is pictured as a spring with force constant k which results in a restoring force $f = -kq$ when the bond is displaced from its equilibrium position by an amount q . In terms of the displacement co-ordinate q , the potential energy can be written as

$$V = 1/2 kq^2 \quad (1)$$

When this is substituted into the one-dimensional wave-equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2\Psi}{dq^2} + V\Psi = E\Psi, \quad (2)$$

the wave functions and energy levels can be solved for directly. The well-known result for the vibrational energy levels is

$$E_n = (n + 1/2)\hbar \left(\frac{k}{\mu}\right)^{1/2} \quad n = 0, 1, 2, \dots \quad (3)$$

¹ E. Schrödinger, *Naturwiss.*, 1926, **14**, 664.

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where $\mu = (m_1 m_2) / (m_1 + m_2)$, the reduced mass for the two-particle system. The wave functions are given by

$$\Psi_n = N_n e^{-\alpha q^2/2} H_n(\alpha^{1/2} q) \quad (4)$$

where N_n is the normalisation factor

$$N_n = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^n n!}\right)^{1/2} \quad (5)$$

and $\alpha = (\mu k)^{1/2} / \hbar$. The H_n are the Hermite polynomials which are readily available in mathematics texts or elsewhere.² The first four such functions are

$$H_0(Z) = 1 \quad H_1(Z) = 2Z \quad H_2(Z) = 4Z^2 - 2 \quad H_3(Z) = 8Z^3 - 12Z \quad (6)$$

Figure 1 shows the harmonic oscillator potential function with the lower energy

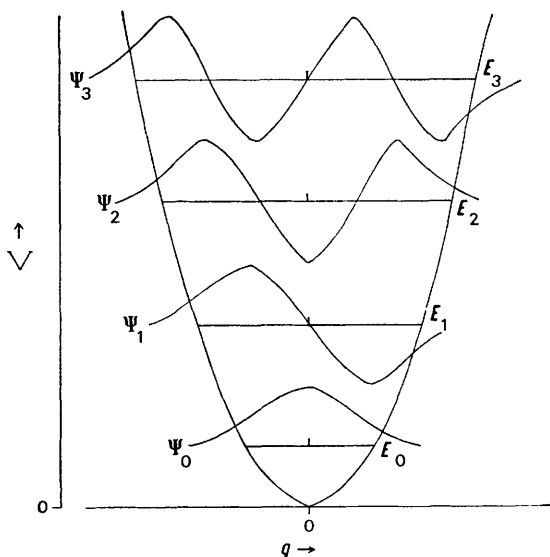


Figure 1 The harmonic oscillator energy levels and wave functions

levels and wave functions superimposed. For many practical purposes the harmonic oscillator approximation leads to a reasonable estimate for the force constant. The observed vibrational frequency ω_e in cm^{-1} is given by

$$\omega_e = \frac{\Delta E}{hc} = \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{1/2} \quad (7)$$

² E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955, p. 289.

This approximation suffers primarily from the fact that $V \rightarrow \infty$ as $q \rightarrow \infty$, whereas for real molecules V asymptotically approaches D_e , the dissociation energy, as q becomes large. As a result, the harmonic oscillator approximation works only for small amplitude vibrations near the bottom of the potential well.

B. The Anharmonic Oscillator.—To correct for the behaviour of the potential energy function at large vibrational displacements, the anharmonic oscillator is often introduced by adding a cubic term (and higher order terms if desired) to the potential function in equation 1. Although this is a somewhat better approximation than the harmonic oscillator, it overcompensates for the error at large values of q and, in fact, $V \rightarrow -\infty$ as $q \rightarrow \infty$. This situation is shown in Figure 2 where the harmonic oscillator and anharmonic oscillator functions are compared to the experimental curve for HCl.

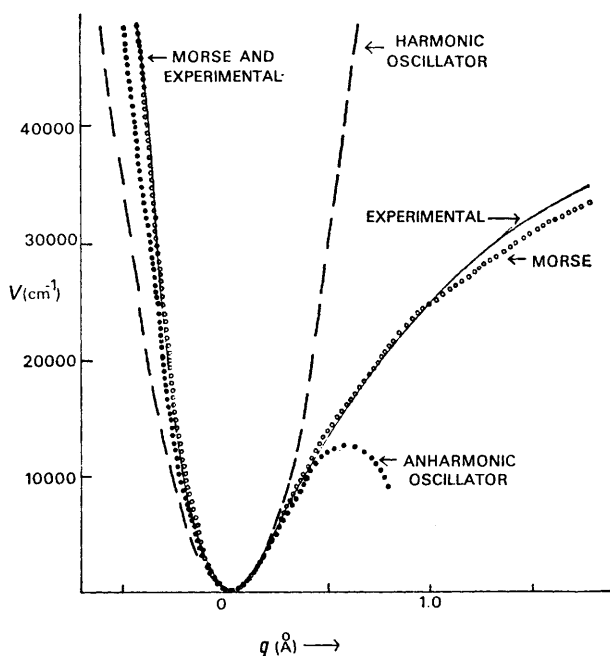


Figure 2 The potential curve and approximations for a diatomic molecule (HCl)

The potential energy of the anharmonic oscillator can be written as a Taylor's series

$$V(q) = V_0 + qV_0' + \frac{1}{2!}q^2V_0'' + \frac{1}{3!}q^3V_0''' + \dots \quad (8)$$

where the subscript 0 implies that V and its derivatives are evaluated at $q = 0$, the equilibrium position. The minimum of a potential curve is conventionally set equal to zero so that $V(0) = V_0 = 0$; V_0' is also zero since the first derivative of a function is always zero at a minimum. If we define $k = V_0''$ and $A = V_0'''/6$, we can write the anharmonic potential function as

$$V = 1/2kq^2 + Aq^3 + \dots \text{ where } k \gg A \quad (9)$$

Fourth and higher power terms could be included if desired. In equation 9 the cubic term serves as a perturbation on the harmonic oscillator and the energy levels are not very different from those of equation 3. These are conventionally given as

$$E_n = hc\omega_e(n + 1/2) - hc\omega_e x_e(n + 1/2)^2 + \dots \quad (10)$$

where ω_e is given by equation 7 and $\omega_e x_e$ is a *single* constant, much smaller than ω_e . If V_0'''' and higher derivatives are negligible, the anharmonicity constant is given by ³

$$\omega_e x_e = \frac{5\hbar}{96\pi c\mu} \left(\frac{V_0''''}{V_0''} \right)^2 = \frac{15}{8} \frac{A^2 \hbar}{\pi c\mu k^2} \quad (11)$$

The constant A in equation 9 is usually negative but $\omega_e x_e$ is positive so that the harmonic oscillator energy levels are decreased somewhat because of the anharmonicity. The observed vibrational fundamental and overtones of HCl can be fitted, to within experimental error, by using $\omega_e = 2988.90 \text{ cm}^{-1}$ ($k = 5.1574 \text{ mdynes/\AA}$) and $\omega_e x_e = 51.60 \text{ cm}^{-1}$.⁴ If no anharmonicity is introduced, the fifth excited state is calculated to be about 1000 cm^{-1} or 8% too high in energy.

C. Other Potential Functions.—A number of other potential functions have been used to approximate the vibrations of diatomic molecules. The most popular of these is the Morse function⁵

$$V(q) = D_e(1 - e^{-aq})^2 \quad (12)$$

where D_e is the dissociation energy and a is a constant characteristic of the molecule in a particular electronic state. The Morse function, which is also shown in Figure 2, matches that of a real molecule in that $V \rightarrow D_e$ as $q \rightarrow \infty$, but V does not approach infinity as it should at zero internuclear distance, $q = -r_e$. This is not a major drawback, however, since the region near $q = -r_e$ is of little practical importance. In terms of equation 8, the Morse potential gives

$$k = 2a^2 D_e, \omega_e = a(\hbar D_e)^{1/2}(\pi c\mu)^{-1/2}, \text{ and } \omega_e x_e = \hbar a^2(4\pi c\mu)^{-1} \quad (13)$$

Since ω_e and $\omega_e x_e$ can be obtained from experimental data by use of equation 10,

³ G. W. King, 'Spectroscopy and Molecular Structure', Holt, Rinehart, and Winston, Chicago, 1964, p. 164.

⁴ G. Herzberg, 'Spectra of Diatomic Molecules', 2nd Edn., Van Nostrand, Princeton, N.J., 1950, p. 55.

⁵ P. M. Morse, *Phys. Rev.*, 1929, **34**, 57.

a and D_e can be calculated from equation 13 to give the Morse curve of equation 12.

Several other functions, most of which contain exponential terms, have also been applied; these include the Ryberg,⁶ Lippincott,⁷ and Varshni⁸ functions. The latter worker has reviewed a number of these functions. One of the best functions from a spectroscopic viewpoint is the modified Morse function,⁹

$$V(q) = D_e[(1 - e^{-aq})^2 + ca^3q^3e^{-2aq}(1 + abq)] \quad (14)$$

where D_e and a are the constants from equation 12 and b and c are other constants that can be expressed in terms of spectroscopic parameters (ω_e , $\omega_e x_e$, D_e , B_e , and α_e).

3 Symmetry Isolated Vibrations

All molecules other than the diatomics must have more than one vibration since $(3N - 6) > 1$ for $N \geq 3$. However, symmetry often plays a rôle in separating the vibrational problem of dimension $3N - 6$ into several sets of vibrations, each of smaller dimension. In several cases only one vibration will have a particular symmetry species and a one-dimensional problem results. For example, the three vibrations for a C_{2v} water molecule have symmetry species $2A_1 + B_1$. Thus the ν_3 mode, the antisymmetric O-H stretching vibration of B_1 symmetry, can be analysed as a one-dimensional system. The one co-ordinate is the appropriate B_1 symmetry co-ordinate,

$$S_3 = \left(\frac{1}{2}\right)^{1/2} (\Delta R_1 - \Delta R_2) \quad (15)$$

where the ΔR_i represent changes in the two O-H bond lengths. Because no other B_1 symmetry co-ordinates can be written, S_3 is necessarily a normal co-ordinate of the molecule. If $Q = S_3$ is the normal co-ordinate, and if we assume a strictly harmonic vibration, we may write

$$-\frac{\hbar^2}{2} \frac{d^2\Psi}{dQ^2} + \frac{1}{2} \lambda Q^2\Psi = E\Psi \quad (16)$$

where $\lambda = 4\pi^2c^2\omega^2 = FG$. F and G are the symmetrised force constant and inverse mass elements used in the Wilson FG method. These can be written as

$$F = F_R - F_{RR} \quad (17)$$

$$G = G_R - G_{RR} = \left(\frac{1}{m_O} + \frac{1}{m_H}\right) - \frac{\cos \alpha}{m_O} \quad (18)$$

where G_R , G_{RR} , F_R , and F_{RR} are the unsymmetrised G and F matrix elements. F_R is the force constant for the O-H bond stretching and F_{RR} is the interaction

⁶ R. Ryberg, *Z. Physik.*, 1931, 73, 376.

⁷ E. R. Lippincott, *J. Chem. Phys.*, 1953, 21, 2070.

⁸ Y. P. Varshni, *Rev. Mod. Phys.*, 1957, 29, 664.

⁹ H. M. Hulburt and J. O. Hirshfelder, *J. Chem. Phys.*, 1961, 35, 1901.

constant for stretching both O–H bonds simultaneously. The m_{O} and m_{H} are the atomic masses of oxygen and hydrogen and α is the value of the HOH equilibrium angle. G can, therefore, be calculated directly from known values. The solution to equation 16 is

$$E = hc\omega = \hbar(GF)^{1/2} \quad (19)$$

and the observed absorption occurs at

$$\omega = (2\pi c)^{-1} (m_{\text{O}}m_{\text{H}})^{-1/2} [(1 - \cos \alpha)m_{\text{H}} + m_{\text{O}}]^{1/2} F^{1/2} \quad (20)$$

Anharmonicity can be introduced into equation 16 by adding to the potential energy terms such as $AQ^3 + BQ^4 + \dots$

Many other molecules in addition to water have only one vibration belonging to a particular symmetry species. The normal vibrations for benzene, for instance, can be described as $2A_{1g} + A_{2g} + 4E_{2g} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2B_{2g} + E_{1g} + A_{2u} + 2E_{2u}$. Consequently, the inactive A_{2g} in-plane C–H wag and the i.r. active A_{2u} out-of-plane C–H bending vibrations can be treated as one-dimensional situations. Another example of a symmetry isolated vibration comes from methane which has vibrations of symmetry species $A_1 + E + 2T$. The A_1 symmetric C–H stretching mode can be studied as a one-dimensional problem; this is an i.r. inactive but Raman active vibration. In general, the molecules which yield one-dimensional vibrations resulting from symmetry isolation are either those with few atoms or those with high symmetry. Among these are Cl_2O , HgCl_2 , SO_2 , BF_3 , N_2O_2 , SiH_4 , BrF_5 , and SF_6 .

In a large number of cases symmetry isolated vibrations possess no special properties and are, therefore, not given any preferential treatment in an analysis. Since they are one-dimensional, however, it would be much easier to analyse in detail the nature of their potential functions.

4 High-frequency Separation

In a number of polyatomic molecules a high-frequency vibration can be treated as a one-dimensional system on the basis that it is only very slightly affected by all the other vibrational modes. For instance, the C–H stretching motion in $\text{CHBr}_2\text{CBr}_3$ will give rise to a vibrational frequency near 2900 cm^{-1} whereas none of the other vibrations have absorption peaks of even half that frequency. As a result there is virtually no interaction between the C–H stretch and the other molecular motions. The vibrations are therefore best treated as two separate problems—one consisting of seventeen modes, the other of one mode of vibration—rather than one system with eighteen vibrations.

In some cases symmetry works hand-in-hand with the high-frequency separation method to yield several one-dimensional systems. In cyclobutane,¹⁰ for example, there are several unique CH_2 stretching vibrations, each of different symmetry, which can be considered as one-dimensional vibrational problems, e.g. the three A_{1g} vibrations include ν_1 , the CH_2 symmetric (in-phase) stretching

¹⁰ R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, 1963, **39**, 2951.

mode. The interaction force constants involving this vibration can be set equal to zero and hence this mode can be considered as independent from the other two and can be analysed separately.

The high-frequency separation can be demonstrated in a simplified way. Assume we have two vibrations of a particular symmetry, one with a high frequency ($\sim 3000 \text{ cm}^{-1}$) and one with a low frequency (below 1500 cm^{-1}). Associated with the high-frequency mode are the force constant F_H and G matrix element G_H . The other vibration has smaller constants F_L and G_L . Cross-term constants, which are even smaller in magnitude, are F_{HL} and G_{HL} . According to the Wilson FG method our matrices are

$$F = \begin{bmatrix} F_H & F_{HL} \\ F_{HL} & F_L \end{bmatrix} \quad \text{where } F_H > F_L > F_{HL} \quad (21)$$

and

$$G = \begin{bmatrix} G_H & G_{HL} \\ G_{HL} & G_L \end{bmatrix} \quad \text{where } G_H > G_L > G_{HL} \quad (22)$$

The secular equation is

$$\begin{vmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{vmatrix} = 0 \quad (23)$$

where

$$\begin{aligned} H_{11} &= F_H G_H + F_{HL} G_{HL} & H_{12} &= F_H G_{HL} + F_{HL} G_L \\ H_{21} &= F_{HL} G_H + F_L G_{HL} & H_{22} &= F_{HL} G_{HL} + F_L G_L \end{aligned} \quad (24)$$

Since by far the largest term is $H_{11} \simeq F_H G_H$, the higher frequency solution can be approximated as $\lambda \simeq H_{11} \simeq F_H G_H$. Since $\lambda^{1/2} = 2\pi c\omega$, for a separable C-H stretching mode we can write

$$\begin{aligned} \omega &= (2\pi c)^{-1} (F_H G_H)^{1/2} = (2\pi c)^{-1} [F_{CH}(m_H^{-1} + m_C^{-1})]^{1/2} \\ &= (2\pi c)^{-1} F_{CH}^{1/2} \mu_{CH}^{-1/2} \end{aligned} \quad (25)$$

This is the result that is obtained from a simple two-atom harmonic oscillator approximation. In chloroform (CHCl_3), for example, the C-H stretching frequency has been observed at 3019 cm^{-1} . The force constant calculated from this number by use of equation 25 is 4.98 mdynes/\AA . A more complete analysis including interaction constants¹¹ gives 4.85 mdynes/\AA , confirming that the high-frequency separation method can give good approximations. The overtones for the chloroform C-H stretching mode have been observed¹² near 5900 , 8700 , $11\,315$, $13\,860$, and $16\,300 \text{ cm}^{-1}$. If equation 10 is used with $\omega_e = 3145$ and $\omega_e x_e = 63 \text{ cm}^{-1}$, the anharmonicity can be accounted for quite accurately on

¹¹ N. B. Colthup, L. H. Daly, and S. E. Wiberly, 'Introduction to Infrared and Raman Spectroscopy', Academic Press, New York, 1964, p. 452.

¹² Reference 4, p. 316.

the basis of the one-dimensional model. This simplified model can also be used to calculate isotopic shifts. For instance, a C-D stretching frequency can be estimated from

$$\frac{\nu_{\text{CH}}}{\nu_{\text{CD}}} = \frac{(2\pi)^{-1}F_{\text{CH}}^{1/2}\mu_{\text{CH}}^{-1/2}}{(2\pi)^{-1}F_{\text{CH}}^{1/2}\mu_{\text{CD}}^{-1/2}} = \frac{m_{\text{D}}(m_{\text{C}} + m_{\text{H}})^{1/2}}{m_{\text{H}}(m_{\text{C}} + m_{\text{D}})} = 1.362 \quad (26)$$

The observed isotopic shifts upon deuterium substitution are generally very close to this value.

One specific situation in which one-dimensional potential functions resulting from a high-frequency separation can be very valuable are in studies of hydrogen-bonded systems.¹³ A function of the type

$$V(x) = \sum_{i=2}^4 a_i x^i \quad (27)$$

where x is a measure of hydrogen-bonded distance and each a_i is a constant, can be used to represent both symmetric or asymmetric potential functions. Unfortunately, the experimental data for systems of this type are not very extensive.

5 Low-frequency Separation

When one vibration has a much lower frequency than all of the others in a molecule, it can be isolated using the low-frequency separation method. This is analogous to the high-frequency method; in fact, it can be pictured that all of the higher frequency modes are separated from the low-frequency mode by use of the high-frequency separation method. If this is done for equation 23, removal of the high-frequency mode results in $\lambda \simeq H_{22} \simeq F_{\text{L}}G_{\text{L}}$ as the solution for the low energy vibration if the latter is assumed to be strictly harmonic; this is usually *not* the case. Most often these vibrations are highly anharmonic.

The study of isolated low-frequency vibrations has been of considerably greater interest than that of the high-frequency modes. The reason for this is that a large number of quantum levels are populated when their energy separations are small. As a consequence, many vibrational transitions originating from excited states can be observed and a very accurate potential function can be obtained for a vibration associated with low frequencies. Vibrations which can be studied individually, based on the low-frequency separation method, include molecular inversions, internal rotations (torsional vibrations), ring-puckering vibrations, and pseudorotation in ring molecules. Attempts have been made to study the double-minimum potential function for hydrogen bonds, but clear evidence for this has been difficult to find.¹⁴

¹³ R. L. Somarjai and D. F. Hornig, *J. Chem. Phys.*, 1962, **36**, 1980.

¹⁴ A. Finch, P. N. Gates, K. Radcliffs, F. N. Dickson, and F. F. Bentley, 'Chemical Applications of Far-Infrared Spectroscopy' Academic Press, 1970, Chapter 5.

A. Molecular Inversion.—The ammonia molecule has six vibrations ($2A_1 + 2E$). The two vibrations of A_1 symmetry are the symmetric N–H stretching and the molecular inversion modes which are readily separable due to their large energy difference. As a result, ν_2 , the inversion mode shown in Figure 3, can be studied

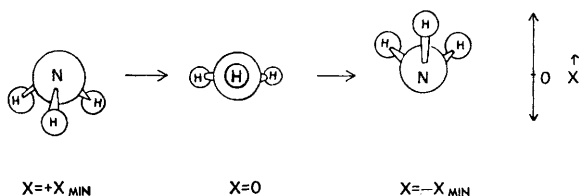


Figure 3 *The molecular inversion vibrational mode in ammonia*

independently as a one-dimensional problem. Since ammonia has two equivalent equilibrium structures of energy lower than the planar form, a double-minimum potential energy function is expected for the inversion. When the potential energy V is plotted vs. x , the inversion co-ordinate ($x = 0$ for the planar structure and $x = \pm x_{\text{min}}$ at equilibrium), the curve shown in Figure 4 results. This has

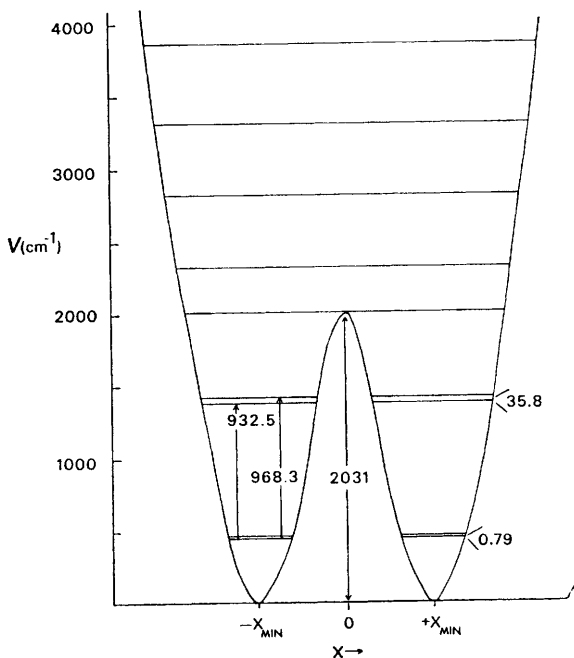


Figure 4 *Potential energy function for the inversion of ammonia*
Data from ref. 18

been found by determining the potential energy function that best fits the observed transitions,¹⁵ which are also shown in the Figure. Several types of functions will yield the curve in Figure 4, including the Manning potential¹⁶ and one of the form $V = Ax^4 - Bx^2$.¹⁷ A number of these types of potential functions have been described by Coon and co-workers¹⁸ and by Schutte.¹⁹ The best function appears to be

$$V = Ax^2 + B \exp(-Cx^2) \quad (28)$$

where $A = 1.18$ dyne cm^{-1} , $B = 2.48 \times 10^{-12}$ erg, and $C = 4.89 \times 10^{16}$ cm^{-2} . The above potential corresponds to a barrier of inversion of 2022 cm^{-1} or 6.78 kcal mol^{-1} . The spectra of ND_3 , NH_2D , and NHD_2 are also well fitted with a similar potential function. The energy levels are different, of course, since the reduced masses used in the one-dimensional wave equation 2 are different.

The NH_2 wagging mode of cyanamide (H_2NCN) has also been studied. Only three transitions were observed for this compound and two others for D_2NCN .²⁰ The data were analysed in terms of the Manning potential

$$V(x) = (k\rho)^{-1} [-(A + D) \text{sech}^2(2\rho)^{-1}x + D \text{sech}^2(2\rho)^{-1}x] \quad (29)$$

where $k = 4\pi c\mu\hbar^{-1}$ and A , D , and ρ are constants. Although equation 29 fits the available data quite accurately, it is not clear whether a potential function with as many adjustable parameters is needed. Equation 29 represents a double-minimum potential with a barrier of 660 cm^{-1} (2.9 kcal mol^{-1}) at the planar configuration. Microwave data on formamide (H_2NCHO) suggest a similar potential may be present in this molecule, with a barrier of 370 cm^{-1} (1.1 kcal mol^{-1}).²¹

B. Internal Rotation.—It is well known that in molecules such as ethane, methyl silane, and methylamine the stable configuration of the molecule is the staggered one; the configuration with the hydrogen atoms eclipsed normally lies a few kcal higher in energy. One of the vibrations in such molecules is the torsion or internal rotation, which is shown for methyl silane in Figure 5. Although

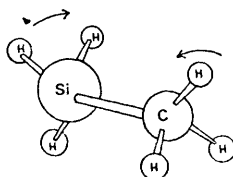


Figure 5 The internal rotation (torsion) vibration in methyl silane

¹⁵ W. S. Benedict and E. L. Player, *Canad. J. Phys.*, 1957, **35**, 1235.

¹⁶ M. F. Manning, *J. Chem. Phys.*, 1935, **3**, 136.

¹⁷ J. Laane, *Appl. Spectroscopy*, 1970, **24**, 73.

¹⁸ J. B. Coon, N. W. Naugle, and R. D. McKenzie, *J. Mol. Spectroscopy*, 1966, **20**, 107.

¹⁹ C. J. H. Schutte, *J. Chem. Educ.*, 1968, **45**, 567.

²⁰ W. H. Fletcher and F. B. Brown, *J. Chem. Phys.*, 1963 **39**, 2478.

²¹ C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, 1960, **32**, 158.

normally the molecule will vibrate near its equilibrium position, at times the amplitude of the vibration becomes sufficiently large to change the molecule from one staggered form to another. This requires crossing the energy barrier at the eclipsed configuration. The potential energy for the vibration in ethane is shown in Figure 6 in terms of ϕ , the angle between the hydrogens in adjacent CH_3 groups ($\phi = 0, 120, 240, 360^\circ$ for eclipsed configurations and $\phi = 60, 180, 300^\circ$ for staggered configurations). Although, in principle, the torsional vibration in ethane is i.r. inactive, a few of the transitions have been observed in the far-i.r. spectrum of a sample under high pressure (7 atm).²² The energy levels and transi-

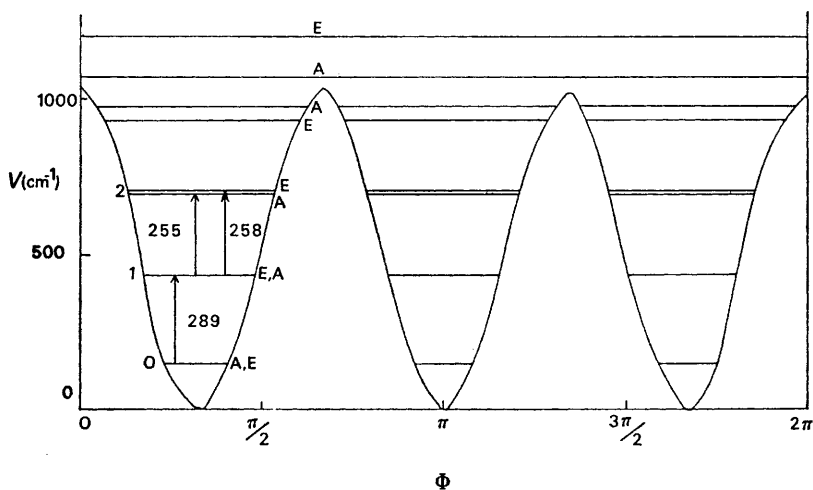


Figure 6 Potential energy function and energy levels for the internal rotation in ethane. Data from ref. 22

tions derived from this work are also shown in Figure 6. The potential energy function used to describe the vibration of internal rotation has the form

$$V = 1/2 \sum_n V_n (1 - \cos n\phi) \quad (30)$$

where only the terms $n = N, 2N, 3N, \dots$ are used for an N -fold rotor. Thus, for a three-fold rotor such as ethane, the V_3 term is by far the most important although a V_6 term may contribute slightly. When higher order terms are small, as is usually the case, the V_3 term is effectively a measure of the barrier to internal rotation. For ethane this is 1024 cm^{-1} or $2.93 \text{ kcal mol}^{-1}$. The internal rotation of many other molecules has also been studied by either far-i.r. or microwave

²² S. Weiss and G. E. Leroi, *J. Chem. Phys.*, 1968, **48**, 962.

spectroscopy. In each case the vibrational energy levels can be obtained by solving the wave equation

$$-B \frac{d^3\Psi}{d\psi^3} + V\Psi = E\Psi \quad (31)$$

where $B = \hbar^2(2rI_a)^{-1}$ is the internal rotation constant which can be calculated from the molecular structure; V is given by equation 30. Much of the theoretical and experimental work done on internal rotation barriers has been summarised in several reviews.²³⁻²⁷ Some of the available data are shown in Table 1.

Table 1 Some three-fold barriers to internal rotation^a

Molecule	Barrier (kcal mol ⁻¹)	Molecule	Barrier (kcal mol ⁻¹)
MeCH ₃	2.93	MeCOOH	0.48
MeNH ₂	1.98	EtI	2.40
MeOH	1.07	EtBr	3.57
MeSH	1.27	EtCl	3.56
MeSiH ₃	1.60	EtF	3.31
MeGeH ₃	1.24	MeCHF ₂	3.18
CH ₂ =CHSiH ₃	1.50	Me ₂ CO	0.76
CH ₂ =CHMe	1.98	Me ₂ O	2.72
MeCHO	1.15	MeSiH ₂	1.67

^a From references 21—26.

The internal rotation of hydrogen peroxide presents one of the more interesting cases.^{28,29} The equilibrium structure of the molecule has a dihedral angle of 111°. The *trans* form lies 1.1 kcal higher and the *cis* lies 7.1 kcal higher still. Figure 7 shows the potential energy curve and vibrational energy levels for the internal rotation of H₂O₂.

C. Ring Puckering.—A saturated four-membered ring molecule and a five-membered ring with one double bond each have an out-of-plane vibration which causes the ring to invert from one configuration to another equivalent one. This vibration yields a large amount of information on molecular structure and forces and has been extensively studied for derivatives of cyclobutane and cyclopentene; it is shown in Figure 8 for the parent compounds.

Some years ago it was postulated that these ring-puckering vibrations should have potential energy functions which are governed by quartic (x^4) terms rather

²³ E. B. Wilson, *Adv. Chem. Phys.*, 1959, **II**, 367.

²⁴ W. H. Flygare, *Ann. Rev. Phys. Chem.*, 1967, **18**, 325.

²⁵ J. E. Williams, P. J. Stang, and P. von R. Schleyer, *Ann. Rev. Phys. Chem.*, 1968, **19**, 531.

²⁶ C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, 1959, **31**, 841.

²⁷ R. A. Pethrick and E. Wyn-Jones, *Quart. Rev.*, 1969, **23**, 301.

²⁸ R. L. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, 1965, **42**, 1931.

²⁹ R. L. Hunt and R. A. Leacock, *J. Chem. Phys.*, 1966, **45**, 3141.

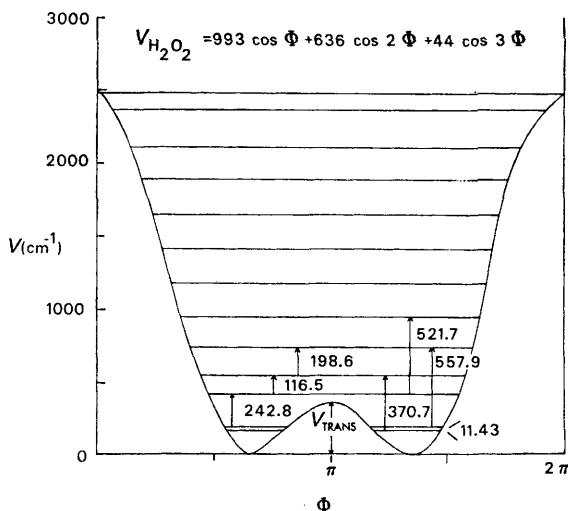


Figure 7 Internal rotation potential energy function of hydrogen peroxide
Data from ref. 28

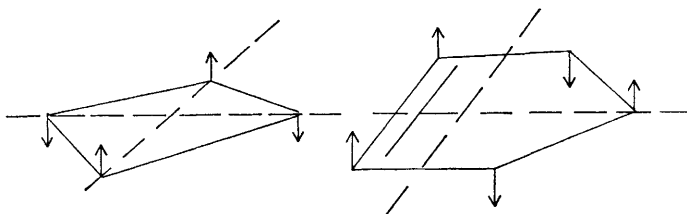


Figure 8 The ring-puckering vibration for (a) cyclobutane and (b) cyclopentene

than the usual quadratic ones. This is because the restoring force of the vibration depends on the ring angle bending forces. It can be shown that these angles ϕ_i are related to the ring puckering co-ordinate x , the displacement of the ring from its planar configuration, by $\Delta\phi_i \approx x^2$. The potential energy of the vibration depends on $(\Delta\phi_i)^2$, i.e. it must depend on x^4 . This prediction has been confirmed in recent years although it has been found that it is desirable to include an additional smaller quadratic term in the potential to match experimental observations. Furthermore, the potential function

$$V = Ax^4 + Bx^2 \quad (32)$$

where A and B are force constants, has the advantage that it can be used to describe the vibration for both planar and non-planar ring systems. If B is positive or zero, the ring is planar; if B is negative the ring is puckered with a barrier to inversion of $B^2/4A$. A is primarily a measure of the angle strain in the

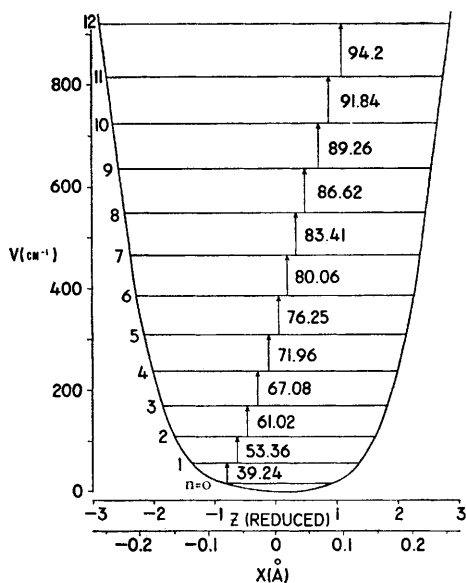


Figure 9 Ring-puckering potential energy function for a planar molecule, silacyclopent-3-ene
From ref. 30

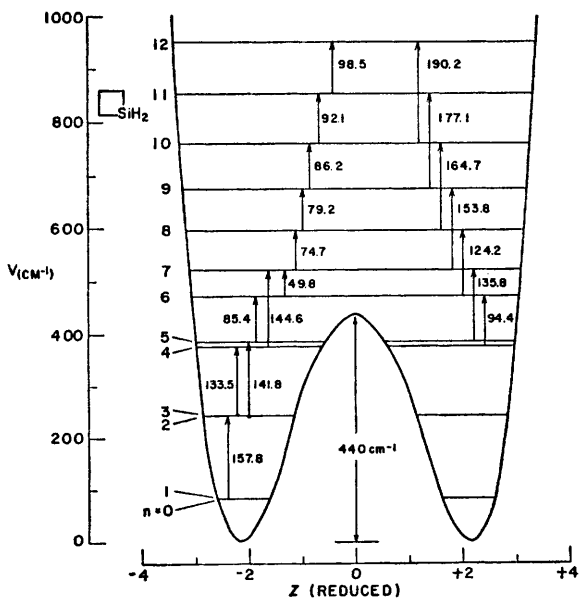


Figure 10 Ring-puckering potential energy function for a non-planar molecule, silacyclobutane
From ref. 31

system which tends to maintain a planar ring; *B* results from the barriers to internal rotation about the individual bonds in a ring that generally try to twist the ring into a puckered configuration.³⁰ Figures 9 and 10 show the potential energy functions and some of the observed far-i.r. transitions for silacyclopent-3-ene³⁰ and silacyclobutane.³¹ The former is a planar molecule; the latter is puckered. The spectrum for the four-membered ring is shown in Figure 11.

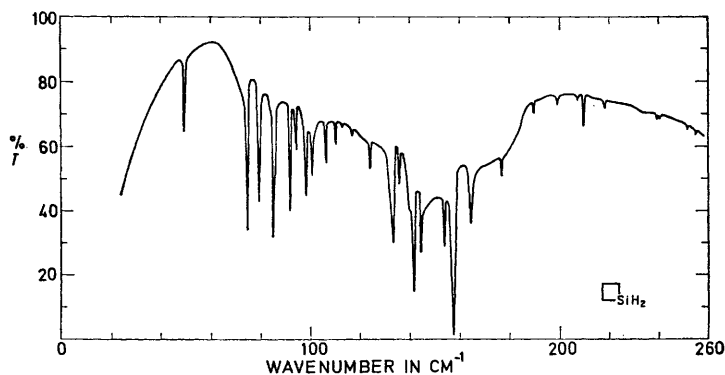





Figure 11 Far-i.r. spectrum of silacyclobutane
From ref. 31

Table 2 Barriers to inversion (kcal mol^{-1}) for ring molecules^a

<i>M</i>			
CH ₂	1.46	0.66	0.66
O	0.04	0	0.24
S	0.78	0	0.68
Se	1.07	—	—
SiH ₂	1.26	0	0
C=O	0.01	—	—
CF ₂	0.69	—	—
C=CH ₂	0.46	—	—
NH	$\left\{ \begin{array}{l} 1.26^b \\ 0.99 \end{array} \right.$	0.16 ^b	—

^a From references 17, 32, and 38; $1 \text{ kcal mol}^{-1} = 350 \text{ cm}^{-1}$.

^b Asymmetric potential function.

Table 2 summarises some of the data that have been obtained from the far-i.r. spectra of four- and five-membered ring molecules.^{17,32} Each spectrum was

³⁰ J. Laane, *J. Chem. Phys.*, 1969, **50**, 776.

³¹ J. Laane and R. C. Lord, *J. Chem. Phys.*, 1968, **48**, 1508.

³² J. Laane, *J. Chem. Phys.*, 1970, **52**, 358.

analysed by use of equation 32 in a one-dimensional Schrödinger equation 2. The reduced mass for the vibration needed for the calculations can be determined from the molecular structure. The potential energy function for each molecule not only makes it possible to determine the energy difference between planar and puckered forms, but also determines the configuration of each molecule. Silacyclobutane, for instance, has a dihedral angle of 36° .

In addition to far-i.r. spectroscopy, microwave spectroscopy has been used the most to study ring-inversion vibrations.^{33,34} Difference band spectra^{35,36} have also been utilised and very recently laser Raman spectroscopy has also been applied to the problem.³⁷ A comprehensive review on ring-puckering has now been prepared.³⁸

D. Pseudorotation.—Saturated five-membered ring molecules undergo a unique type of vibration known as pseudorotation.^{39–41} This phenomenon has recently been the subject of a review.⁴² Although ring molecules of this type have *two* low frequency vibrations, these are separable into modes of different symmetry. The pseudorotation, which looks like an amplitude wave travelling about the ring, can then be studied as a one-dimensional system according to

$$-B \frac{d^2\Psi}{d\phi^2} + \frac{1}{2} \sum_n V_n (1 - \cos n\phi) \Psi = E\Psi \quad (33)$$

where B is a pseudorotation constant and ϕ is a phase parameter. For cyclo-

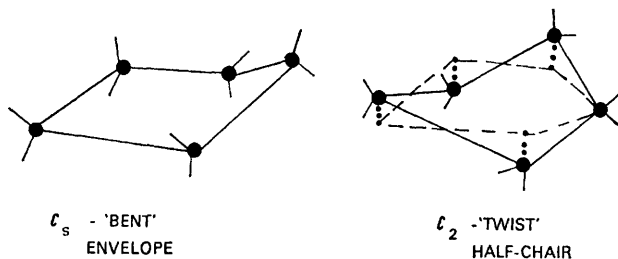


Figure 12 Conformations of cyclopentane

³³ D. O. Harris, H. W. Harington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, 1966, **44**, 3467.

³⁴ L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 1968, **49**, 3041.

³⁵ T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, 1968, **49**, 470.

³⁶ T. B. Malloy, F. Fisher, and R. M. Hedges, *J. Chem. Phys.*, 1970, **53**, 5325.

³⁷ F. A. Miller and R. J. Capwell, to be published.

³⁸ C. S. Blackwell and R. C. Lord, *Appl. Spectroscopy Rev.*, to be published.

³⁹ J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483; 1958, **80**, 6697.

⁴⁰ K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 1959, **81**, 3214.

⁴¹ D. O. Harris, *et al.*, *J. Chem. Phys.*, 1969, **50**, 2438.

⁴² J. Laane, *Appl. Spectroscopy Rev.*, to be published.

pentane $\phi = 0, \pi/5, 2\pi/5, \dots, 2\pi$ correspond to bent (envelope) forms of the molecule and $\phi = \pi/10, 3\pi/10, \pi/2, \dots, 19\pi/10$ correspond to twist (half-chair) forms. During the vibration, as ϕ changes, the molecule readily converts from one bent form, to a twist form, to another bent form, *etc.* The two configurations are shown for cyclopentane in Figure 12, and Figure 13 gives the course of the vibration. Since the bent and twist forms of cyclopentane have nearly the same energy, only a very small V_{10} term is expected in equation 33 for this

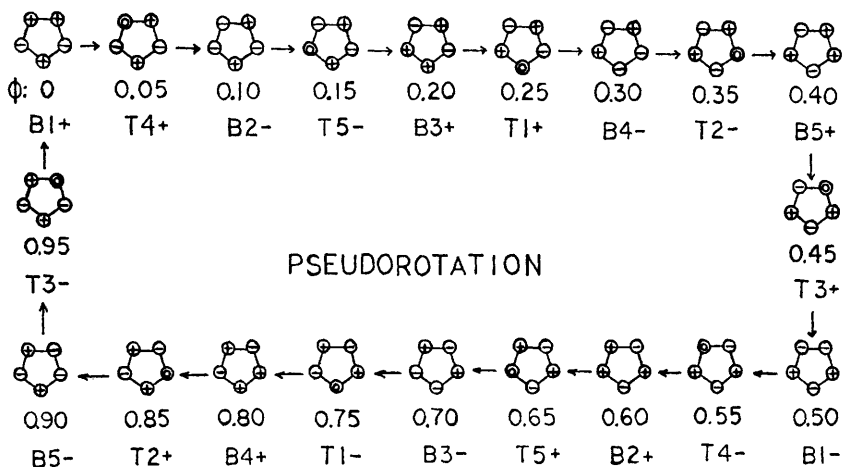


Figure 13 Pseudorotation of cyclopentane. ϕ is given in fractions of a circle

Table 3 Barriers to pseudorotation of five-membered rings^a

Molecule	Barrier (kcal mol ⁻¹)	B (cm ⁻¹)
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$	0	2.5
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}}$	0.14	3.19
$\overline{\text{CH}_2\text{CH}_2\text{OCH}_2\text{O}}$	~0.1	3.99
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{S}}$	2.21	2.35
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_2}$	3.89	1.97
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Se}}$	5.35	1.55
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{GeH}_2}$	5.9	1.5
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}}$	3.72	1.93

^a From reference 42.

molecule. Not all the ring atoms are equivalent for derivatives such as silacyclopentane and thiacyclopentane, hence only $\phi = 0, \pi, 2\pi$ represent bent forms and $\phi = \pi/2, 3\pi/2$ represent twist forms; all other values of ϕ indicate intermediate structures. For these derivatives V_2 terms predominate although V_3 terms may be present. For silacyclopentane V_2 is 1360 cm^{-1} ($3.9 \text{ kcal mol}^{-1}$) and this is a direct measure of the energy difference between the bent (C_n symmetry) and twist (C_2 symmetry) forms, the latter being more stable. Table 3 lists several of the pseudorotation barriers obtained from far-i.r. data.⁴³ A typical one-dimensional potential energy function in terms of ϕ is shown in Figure 14 for silacyclopentane.⁴³

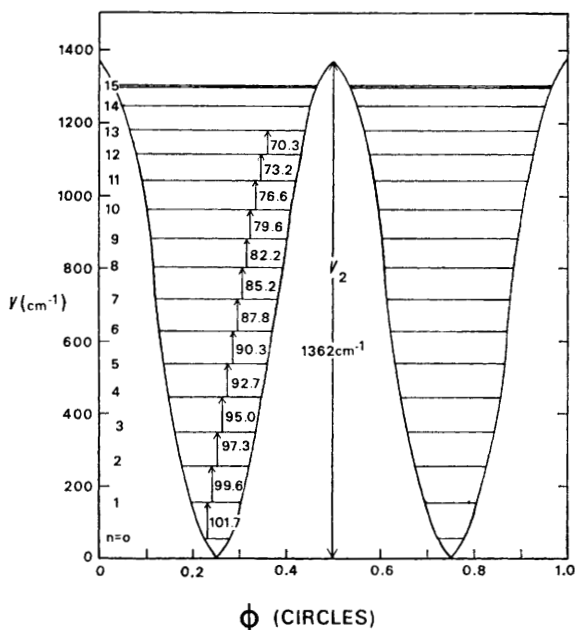


Figure 14 Pseudorotation potential energy function for silacyclopentane
From ref. 43

6 Calculation of Energy Levels

All the important potential energy functions described previously have the form

$$V = \sum_n a_n x^n \quad (34)$$

or

$$V = \frac{1}{2} \sum_n V_n (1 - \cos n\phi) \quad (35)$$

⁴³ J. Laane, *J. Chem. Phys.*, 1969, **50**, 1946.

although equation 34 may have an extra Gaussian term [$b \exp(-cx^2)$] added. Except for the simple harmonic oscillator case where $V = \frac{1}{2}kx^2$, the energy levels for these potential functions cannot be solved from the wave equation in closed form. Approximation techniques are necessary to obtain the levels. The potential function in equation 34 has been discussed in detail and tables of energy levels are available.³² A similar discussion will appear for the potential of equation 35.⁴⁴ Although a number of techniques have been used, the best method for calculating energy levels appears to be the use of harmonic oscillator basis functions for equation 34 and the sin-cos basis functions for equation 35.⁴⁵ In brief, the method is to set up first the Hamiltonian in the suitable basis representation and then diagonalise the resultant matrix. The diagonalisation yields both the eigenvalues (energy levels) and eigenvectors (wave functions).

As an example, for the potential function $V = (1/2)V_2(1 - \cos 2\phi)$ the Hamiltonian is

$$H = -d^2/d\phi^2 + (V_2/2B)(1 - \cos 2\phi) \quad (36)$$

and the appropriately dimensioned energy levels E are given in terms of the eigenvalues λ by $E = B\lambda$. The Hamiltonian matrix is set up in both the sin and cos representations in order to obtain 'odd' and 'even' levels respectively. The matrices have the form

$$\begin{bmatrix} H_{11} & H_{12} & \cdot & \cdot & \cdot & H_{1N} \\ H_{21} & H_{22} & \cdot & \cdot & \cdot & H_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ H_{N1} & H_{N2} & \cdot & \cdot & \cdot & H_{NN} \end{bmatrix} \quad (37)$$

where N is the number of basis functions used. The elements of the matrix are given by

$$H_{kl} = \int \Psi_k^* H \Psi_l d\tau \quad (38)$$

where Ψ_k and Ψ_l are the basis functions given by

$$\Psi_m = \pi^{-1/2} \sin m\phi \quad (39)$$

for the sin functions and by

$$\Psi_m = \pi^{-1/2} \cos m\phi \quad (40)$$

for the cos functions. Use of equations 36—39 gives the following Hamiltonian matrix in the sin representation for the two-fold potential

⁴⁴ J. D. Lewis, T. B. Malloy, and J. Laane, to be published.

⁴⁵ D. O. Harris, G. G. Engerholm, and W. D. Gwinn, *J. Chem. Phys.*, 1965, **43**, 1515.

$$\begin{bmatrix} 1 + S_2 & 0 & -S_2/2 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 4 + S_2/2 & 0 & -S_2/2 & \cdot & \cdot & \cdot & 0 \\ -S_2/2 & 0 & 9 + S_2/2 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & -S_2/2 & 0 & 16 + S_2/2 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \cdot & \cdot & \cdot & N^2 + S_2/2 \end{bmatrix} \quad (41)$$

where $S_2 = V_2/2B$. The cos matrix is similar.

For potential functions having the form of equation 35, harmonic oscillator basis functions based on the Hermite polynomials are used. The individual H_{kl} elements are calculated from equation 38 by use of $\Psi_m = \Psi_{m-1}^{\text{H.O.}}$. That is, Ψ_1 is the ground state wave function of the harmonic oscillator, Ψ_2 is that for the first excited state, and so on.

After the Hamiltonian matrix has been set up, the eigenvalues ($\lambda = E/B$) and eigenvectors (wave functions) can be obtained by diagonalising the matrix.⁴⁶ This is a common procedure for a computer calculation and a number of data processing centres have it available as a standard subroutine.

The energy levels resulting from the Hamiltonian in equation 36 have been tabulated in 'Mathieu tables' but these do not make it possible to work with the more general potential function in equation 35.

7 Conclusion

A number of situations give rise to one-dimensional vibrational problems. Of these, the low energy modes studied by far-i.r. spectra can lead to the most valuable information. The spectra can be analysed in terms of either power series or periodic potential energy functions. The energy levels for these functions are best obtained using matrix diagonalisation techniques.

The author wishes to thank the Robert A. Welch Foundation for supporting his research on low-frequency vibrations.

⁴⁶ A. Ralston, 'A First Course in Numerical Analysis', McGraw-Hill, New York, 1965, Chapter 10.