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Density of levels in vibrational spectra of molecules

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Abstract

Density distribution of the discrete spectrum of a Hamiltonian which represents a system of N coupled oscillators and, hence, may describe molecular vibrations in the local mode approximation, is analyzed. The spectral density moments are expressed as linear combinations of products of coefficients which depend on the molecular topology (analogs of the propagation coefficients in the statistical theory of nuclear and atomic spectra) and of one-particle moments describing individual bonds and interactions between them. The dependence of the first three moments of the energy level density on the structural parameters of the molecule is discussed. Detailed expressions for several special cases are derived.

I. INTRODUCTION

Statistical spectroscopy has mainly been applied to studies on nuclear and atomic spectra¹⁻⁵. Its usefulness to studying vibrational spectra of molecules has been appreciated rather recently⁶⁻¹⁰. On the other hand, statistical spectroscopy is very well suited to describing properties of vibrational and ro-vibrational molecular spectra. The molecular spectra are composed of many densely-packed levels. Therefore, frequently, some information about a general shape of the spectrum rather than about its detailed structure is required. Also the exact form of the Hamiltonian, particularly in cases of polyatomic molecules, is unknown. All these features of the vibrational spectra make them a perfect goal to statistical studies.

Very recently expressions for moments of the spectral density distribution of an N -particle Hamiltonian describing a system of coupled oscillators have been derived¹¹. In the final formulas the N -body moments are expressed as linear combinations of products of the primitive one-body moments. The coefficients of the combinations contain information about structure of the molecule, while the one-body moments describe individual bonds and pair interactions between them.

In the present work the first three moments, i. e. the average energy, the width of the spectrum and its skewness, are studied in detail. In effect the densities of the vibrational levels are expressed as explicit functions of the structural parameters of the molecule. The formulas are directly applicable to estimate the density distributions of specific spectra.

II. OPERATORS AND THEIR MOMENTS

We assume that the vibrational Hamiltonian H of a molecule is expressed in the local mode approximation. Then,

$$H = H'_0 + H'_1 \quad (1)$$

where

$$H'_0 = \sum_{k=1}^N h'_k(k) \quad (2)$$

represents the one-body part, and

$$H'_1 = \sum_{k>l}^N \Lambda_{kl} f'_k(k) f'_l(l) \quad (3)$$

describes interactions. The one-body operators

$$h'_k(k) = \frac{p(k)^2}{2m_k} + V_k(k), \quad (4)$$

where m_k is the reduced mass of the bond k and $V(k)$ is the bond potential (as e.g. the harmonic oscillator or the Morse potential), correspond to individual bonds. The two-body operators describe interactions between the bonds. The interaction terms are defined as bilinear forms of one-body operators. Usually $f'(k)$ are taken as combinations of the momentum operators (the kinetic

coupling) and/or of powers of the corresponding coordinate¹⁰. In the simplest case they may be put equal to the coordinates.

The matrix $\mathbf{\Lambda}$ in the interaction term reflects the structural properties of the molecule. It is closely related to the topological matrix^{12,13}. Its elements are numbered by the molecular bonds and are equal to the interaction constants Λ_{kl} . By definition $\Lambda_{kl} = \Lambda_{lk}$ and $\Lambda_{kk} = 0$. If only adjacent bonds are assumed to interact and if all the interaction parameters are the same and equal λ , then

$$\mathbf{\Lambda} = \lambda \mathbf{T}, \quad (5)$$

where \mathbf{T} is the topological matrix of the molecular bonds. The elements of \mathbf{T} are 1 for the adjacent bonds and 0 otherwise.

We assume that h'_k have finite and discrete spectra, i.e.

$$h'_k |k_p\rangle = \varepsilon'_p |k_p\rangle, \quad p = 1, 2, \dots, d_k, \quad k = 1, 2, \dots, N \quad (6)$$

with $\langle k_p | k_q \rangle = \delta_{pq}$. If the one-body Hamiltonians have infinite spectra (as e.g. the harmonic oscillators) or contain continuum (as e.g. the Morse oscillators) then h'_k are their projections to appropriate finite dimensional spaces. The projections are aimed at removing the “unphysical” parts of the spectra.

The total Hamiltonian is defined in a finite-dimensional model space spanned by a set of orthogonal products of eigenfunctions of the one-body operators. The basis vectors of the model space are defined as

$$|L\rangle = \prod_{k=1}^N |k_{p(L)}\rangle. \quad (7)$$

The dimension of the model space is given by

$$D = \prod_{k=1}^N d_k. \quad (8)$$

The average value of an one-particle operator g'_k , which depends upon the coordinates of the bond k , is defined as

$$\overline{g'_k} = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | g'_k | k_p \rangle \quad (9)$$

It is convenient to redefine the one-body operators so that their average values vanish. Then, we define

$$g_k(k) = g'_k(k) - \overline{g'_k}, \quad (10)$$

Expressions (2) – (4) appearing in Hamiltonian (1) may be rearranged in such a way that they are expressed in terms of the traceless operators H_0 , H_1 , h_k , and f_k . Then,

$$H = \overline{H} + H_0 + H_1, \quad (11)$$

where

$$\overline{H} = \frac{1}{D} Tr H = \sum_{k=1}^N \overline{h'_k} + \sum_{k>l}^N \Lambda_{kl} \overline{f'_k} \overline{f'_l}. \quad (12)$$

is the average energy of the system,

$$H_0 = \sum_{k=1}^N h_k(k), \quad (13)$$

$$H_1 = \sum_{k>l}^N \Lambda_{kl} f_k(k) f_l(l), \quad (14)$$

and

$$f_k(k) = f'_k(k) - \overline{f'_k}, \quad (15)$$

$$h_k(k) = h'_k(k) - \overline{h'_k} + f_k(k) \sum_l^N \Lambda_{kl} \overline{f'_l}. \quad (16)$$

If the origin of the energy scale is chosen so that $\overline{H} = 0$, then the q -th moment of the Hamiltonian spectral density distribution is given by

$$M_q = \frac{1}{D} \sum_L^D \langle L | (H_0 + H_1)^q | L \rangle, \quad (17)$$

After some algebra¹¹, the N -particle moments M_q may be expressed in terms of the one-particle ones:

$$\mu_q(h_k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | h_k^q | k_p \rangle, \quad (18)$$

$$\mu_q(f_k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | f_k^q | k_p \rangle, \quad (19)$$

and

$$\mu_{qr}(h_k f_k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | h_k^q f_k^r | k_p \rangle. \quad (20)$$

If the operators h_k and f_k do not commute (as it is usually) then $\mu_{qr}(h_k f_k)$ is defined as the arithmetic average over all $\binom{q+r}{q}$ different products of them.

III. THE FIRST THREE MOMENTS

The position of the spectrum and its general shape is determined by the first three moments of the spectral density distribution. The first moment, i.e. the average energy \overline{H} , defines the location of the spectrum. It is given by Eq. (12). In order to describe the shape of the spectral density, it is most convenient to set the origin of the energy scale so that $\overline{H} = 0$. It is assumed hereafter that $\overline{H} = 0$.

The second moment, M_2 , gives the width of the spectrum. According to Eqs. (66) - (69) of Ref. 11 we get

$$M_2 = \sum_{k=1}^N \mu_2(h_k) + \frac{1}{2} \sum_{kl}^N \Lambda_{kl}^2 \mu_2(f_k) \mu_2(f_l). \quad (21)$$

As one can see, all quantities in this equation are positive. In order to compare different spectra, one can select the energy units so that $M_2 = 1$. A spectrum for which $M_1 = 0$ and $M_2 = 1$ is referred to as *normalized*.

The third moment determines the asymmetry of the spectrum. If the spectral density is symmetric relative to the average energy then $M_3 = 0$. If the distances between the adjacent levels decrease when their energy increases (as it is in the case of the discrete spectrum of the Morse oscillator), then $M_3 < 0$. For the spectrum in which the distances increase with increasing energies (as e.g. in the case of the spectrum of an infinite potential well), then $M_3 > 0$. The third moment may be obtained from Eqs. (67) - (72) of Ref. 11 and reads

$$M_3 = \sum_{k=1}^N \mu_3(h_k) + 3 \sum_{kl}^N \Lambda_{kl} \mu_{11}(h_k f_k) \mu_{11}(h_l f_l) + 3 \sum_{kl}^N \Lambda_{kl}^2 \mu_{12}(h_k f_k) \mu_2(f_l) + \frac{1}{2} \sum_{kl}^N \Lambda_{kl}^3 \mu_3(f_k) \mu_3(f_l) + \sum_{klm}^N \Lambda_{kl} \Lambda_{lm} \Lambda_{mk} \mu_2(f_k) \mu_2(f_l) \mu_2(f_m) \quad (22)$$

The value of M_3 calculated for the normalized spectrum is called *skewness*. The skewness parameter γ is given by

$$\gamma = M_3 / (M_2)^{3/2}. \quad (23)$$

The moments $\mu_{11}(h_k f_k)$ and $\mu_{12}(h_k f_k)$ may be expressed in the following way:

$$\mu_{11}(h_k f_k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | \frac{1}{2} (h_k f_k + f_k h_k) | k_p \rangle \quad (24)$$

$$= \overline{h_k f_k} = \overline{f_k h_k}, \quad (25)$$

and

$$\mu_{12}(h_k f_k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | \frac{1}{3} (h_k f_k^2 + f_k h_k f_k + f_k^2 h_k) | k_p \rangle \quad (26)$$

Transforming the Eq. (26) one should remember that the basis $\{|k_p\rangle\}_{p=1}^{d_k}$ is not complete and that the operators h_k and f_k do not commute. Then, taking into account the specific form of h_k (Eqs. (4) and (16)) and assuming that f_k is a function of the coordinate x_k , we obtain

$$\mu_{12}(h_k f_k) = \overline{h_k f_k^2} + \frac{1}{6m_k} \overline{\left(\frac{df}{dx_k}\right)^2}. \quad (27)$$

IV. APPLICATIONS

Implementation of this formalism in studies on real molecular systems implies using potential energy surfaces, derived either from the electronic structure calculations or from spectroscopical investigations followed by numerical evaluation of the appropriate one-particle moments. Leaving this kind of advanced numerical studies for some future work, in this paper we present several analytically solvable examples. Our aim is, on one hand, to demonstrate what

kind of problems may be approached using this theory and, on the other, to investigate how the density of vibrational levels depends on the structure of a molecule. The results of this section, though quantitatively do not correspond to any specific molecule, provide qualitative description of variations of the level densities resulting from changes of the molecular topology.

A. Symmetric Bond Potentials

Let us assume that each bond is described by a symmetric potential, i.e. that

$$V_k(x_k^0 + x_k) = V_k(x_k^0 - x_k) \quad (28)$$

where x_k^0 is the value of the coordinate corresponding to the equilibrium bond length and x_k is the distance from the equilibrium. For simplicity we define the bond coordinates so that $x_k^0 = 0$. The most common case is the harmonic oscillator. A more realistic example is a symmetric finite potential well.

Let us also assume that the interactions between bonds are described by bilinear forms of the bond coordinates, i.e. that

$$f_k(k) = x_k - \bar{x}_k \quad (29)$$

(c.f. Ref. 10). In such a case the expectation values of the odd powers of f_k vanish, i.e. $\mu_3(f_k) = \mu_{11}(h_k f_k) = 0$.

If we denote

$$F_{pq} = \mu_2(h_p) \delta_{pq} \quad (30)$$

$$G_{pq} = \mu_3(h_p) \delta_{pq} \quad (31)$$

$$S_{pq} = \mu_2(f_p) \delta_{pq} \quad (32)$$

$$C_{pq} = \mu_{12}(h_p f_p^2) \delta_{pq} \quad (33)$$

then Eqs. (21) and (22) may be, respectively, rewritten as

$$M_2 = Tr[\mathbf{F} + \frac{1}{2}(\mathbf{\Lambda S})^2] \quad (34)$$

$$M_3 = Tr[\mathbf{G} + 3(\mathbf{\Lambda C \Lambda S}) + (\mathbf{\Lambda S})^3] \quad (35)$$

where \mathbf{F} , \mathbf{G} , \mathbf{S} , \mathbf{C} and $\mathbf{\Lambda}$ denote the corresponding matrices.

Matrix elements of \mathbf{F} and \mathbf{S} are always positive (they are sums of squares of real numbers). Since in the expression for M_2 products of elements of \mathbf{S} are multiplied by squares of the coupling constants Λ_{kl} , the width of the spectrum always increases with an increasing complexity of the molecule. Adding new bonds or new bond-bond interaction terms always results in an increase of the second moment of the spectral density distribution.

The third moment, i.e. the asymmetry of the spectral density, behaves in a more complex way. If we assume that

$$\langle k_n | f_k(k)^2 | k_n \rangle < \langle k_{n+1} | f_k(k)^2 | k_{n+1} \rangle,$$

i.e. that the average value of the square of the bond coordinate increases with an increase of the bond excitation energy (and this is the case when taking

any realistic V_k), then the elements of \mathbf{C} are positive. Matrix elements of \mathbf{G} are equal to zero if the energy levels of the single-bond vibrations are equally spaced (harmonic oscillator). If the density of eigenvalues of h_k increases with their increasing values (as it is in most common cases) then the elements of \mathbf{G} are negative. Therefore the first two terms of the rhs of Eq. (35) have usually opposite signs. The third term is either positive (if the coupling constants are all positive) or (in the opposite case) may be negative. However the third term contains only “cyclic” products $\Lambda_{kl}\Lambda_{lm}\Lambda_{mk}$. They vanish, unless the molecule contains three-member cycles of interacting bonds, i.e. if bond k interacts with both l and m while, simultaneously, bonds l and m interact with each other.

Hence, when the bonds do not interact, the asymmetry of the molecular spectrum is negative. It is a sum of asymmetries of the single bond spectra. The interactions would usually reduce this asymmetry. In the case of small asymmetries of the single bond spectra and rather strong coupling between the bonds, the third moment may become positive, i.e. the lower part of the spectrum may become more dense than the upper¹⁴. The trifold cycles of interacting bonds may influence the spectral asymmetry in a relatively strong and specific manner.

The moments may be expressed in a particularly simple way when all bonds are described by the same potential. Then the diagonal elements in matrices \mathbf{F} , \mathbf{G} , \mathbf{S} , and \mathbf{C} are all the same. If we denote them, respectively, f , g , s , and c , then Eqs. (34) and (35) read

$$M_2 = N[f + \frac{1}{2}s^2\mu_2(\mathbf{\Lambda})] \quad (36)$$

$$M_3 = N[g + 3cs\mu_2(\mathbf{\Lambda}) + s^3\mu_3(\mathbf{\Lambda})] \quad (37)$$

where

$$\mu_q(\mathbf{\Lambda}) = \frac{1}{N}Tr(\mathbf{\Lambda}^q) \quad (38)$$

As one can see, the spectral density distribution moments are, in this case, proportional to the number of bonds, with M_3 being negative, positive or zero, depending on the interplay between different parameters.

In order to expose the dependence of M_2 and M_3 on the structural parameters of the molecule, let us assume that only the neighbouring bonds interact and that all the coupling constants are the same and equal λ (Eq. (5)). Then

$$\mu_2(\mathbf{\Lambda}) = \frac{2A_2}{N}\lambda^2 \quad (39)$$

$$\mu_3(\mathbf{\Lambda}) = \frac{6A_3}{N}\lambda^3, \quad (40)$$

where A_2 is the number of pairs of interacting bonds and A_3 is the number of 3-member cycles of interacting bonds. For example, in the case of a linear molecule $A_2 = N - 1$ and $A_3 = 0$; in the case of XY_n -type molecule $A_2 = \binom{N}{2}$ and $A_3 = \binom{N}{3}$; in the case of a ring $A_2 = N$ and $A_3 = \delta_{N3}$, etc. Hence, for a linear molecule

$$M_2 = N[f + s^2\lambda^2(1 - \frac{1}{N})], \quad (41)$$

$$M_3 = N[g + 6cs\lambda^2(1 - \frac{1}{N})]. \quad (42)$$

The corresponding expressions in the case of a ring molecule with $N > 3$, are

$$M_2 = N[f + s^2\lambda^2], \quad (43)$$

$$M_3 = N[g + 6cs\lambda^2]. \quad (44)$$

The difference is more substantial in the case of $N = 3$. For a linear system of three identical atoms

$$M_3 = 3g + 12cs\lambda^2 \quad (45)$$

and for a three-atom ring

$$M_3 = 3g + 18cs\lambda^2 + 6s^3\lambda^3. \quad (46)$$

B. System of Harmonic Oscillators

As a simple exactly solvable model let us consider a system of N harmonic oscillators. Each of them represents a bond. The oscillators are coupled by bilinear function of the vibrational coordinates. The equally spaced energy levels of the bond vibrations

$$\varepsilon'_n{}^k = \omega_k(n + \frac{1}{2}), \quad n = 0, \dots, d_k - 1 \quad (47)$$

spread from $\omega_k/2$ to $\omega_k(d_k - 1/2)$. The average energy is equal to

$$\overline{h'_k} = \frac{D_k}{2}, \quad (48)$$

where

$$D_k = \omega_k d_k. \quad (49)$$

is the ‘‘dissociation energy’’ of the bond. The eigenvalues of h_k are¹⁵

$$\varepsilon_n^k = \omega_k(n + 1/2) - D_k/2. \quad (50)$$

After some simple algebra one gets:

$$\mu_2(h_k) = \frac{D_k^2 - \omega_k^2}{12} \quad (51)$$

$$\mu_3(h_k) = 0 \quad (52)$$

$$\mu_{12}(h_k f_k) = \frac{D_k^2 + \omega_k^2}{12m_k\omega_k^2} \quad (53)$$

$$\mu_2(f_k) = \frac{D_k}{2m_k\omega_k^2}. \quad (54)$$

It is convenient to renormalize the coupling parameters:

$$\tilde{\Lambda}_{kl} = \frac{\Lambda_{kl}}{\omega_k\omega_l(m_k m_l)^{1/2}}. \quad (55)$$

Then the expressions for M_2 and M_3 may be written in a compact form

$$M_2 = \frac{1}{12} \text{Tr}[\mathbf{D}^2 - \boldsymbol{\omega}^2 + \frac{3}{2}(\tilde{\Lambda}\mathbf{D})^2] \quad (56)$$

$$M_3 = \frac{1}{8} \text{Tr}[(\tilde{\Lambda}\mathbf{D})(\mathbf{D}\tilde{\Lambda}\mathbf{D} + \boldsymbol{\omega}\tilde{\Lambda}\boldsymbol{\omega}) + (\tilde{\Lambda}\mathbf{D})^3] \quad (57)$$

where the elements of \mathbf{D} and $\boldsymbol{\omega}$ are, respectively, $D_k\delta_{kl}$ and $\omega_k\delta_{kl}$. The last two formulas result directly from the more general equations (34) and (35). An important difference is, that in the case of a bond described by a harmonic oscillator, the spectrum of h is symmetric and $\mu_3(h)$ vanishes. In consequence M_3 is positive - it depends on the coupling terms only. Therefore the harmonic oscillator expression for M_3 may be used to estimate the correction due to the coupling between bonds rather than to predict asymmetry of a real distribution of the energy levels.

In the case when all D_k and all ω_k are the same and equal, respectively, D and ω , Eqs. (56) and (57) become

$$M_2 = \frac{ND^2}{12} [1 - \omega^2/D^2 + 3\mu_2(\tilde{\Lambda})/2] \quad (58)$$

$$M_3 = \frac{ND^3}{8} [(1 + \omega^2/D^2)\mu_2(\tilde{\Lambda}) + \mu_3(\tilde{\Lambda})] \quad (59)$$

Finally, assuming that all the renormalized coupling constants between the adjacent bonds are equal $\tilde{\lambda}$ while the remaining ones vanish, using Eqs. (39), (40), (58), (59), and neglecting $(\omega/D)^2$ relative to 1, we get simple expressions for the dispersion:

$$\sigma^2 = \frac{ND^2}{12} (1 + \frac{3A_2}{N}\tilde{\lambda}^2) \quad (60)$$

and for the skewness parameter:

$$\gamma = 2 \frac{A_2\tilde{\lambda}^2 + 3A_3\tilde{\lambda}^3}{(A_2\tilde{\lambda}^2 + N/3)^{3/2}}. \quad (61)$$

In the case of linear and ring molecules, for sufficiently large N , $A_2 \approx N$ and $A_3 = 0$. For a graphite-type lattice, $A_2 \approx 3N$ and $A_3 \approx N$. In all these cases, as well as in all realistic large- N molecules, σ is approximately proportional to $N^{1/2}$ and γ — to $N^{-1/2}$.

C. Influence of anharmonicity and asymmetry

More realistic description of a molecule may be given by a system of coupled Morse oscillators. Then, we assume that

$$V_k(x_k) = D_k(1 - e^{-\alpha_k x_k})^2, \quad (62)$$

where D_k is the bond dissociation energy,

$$\alpha_k = (2m_k\omega_k\chi_k)^{1/2}, \quad (63)$$

and

$$\chi_k = \frac{\omega_k}{4D_k}. \quad (64)$$

The discrete energy levels are

$$\varepsilon'_n{}^k = \omega_k(n + 1/2) - \omega_k\chi_k(n + 1/2)^2, \quad n = 0, \dots, d_k - 1, \quad (65)$$

where d_k is the largest integer smaller than $(1 + \chi_k)/2\chi_k$. Therefore, Eq. (49) which links D_k/ω_k with d_k in the case of the harmonic oscillator, for the Morse oscillator reads

$$D_k = \frac{\omega_k}{4}(2d_k - 1). \quad (66)$$

The average energy is equal to

$$\overline{h}_k = \frac{2D_k}{3} + \frac{\omega_k}{12} \quad (67)$$

and the eigenvalues of h_k are

$$\varepsilon_n^k = \omega_k(n + 1/2) - \omega_k\chi_k(n + 1/2)^2 - 2D_k/3 - \omega_k/12. \quad (68)$$

The Schrödinger equation (4) corresponding to the Morse oscillator is solvable analytically and matrix elements appearing in Eqs. (21) and (22) are available in the literature^{16,17}. However the resulting expressions are too complicated to allow for a general and transparent discussion of the influence of the asymmetry and of the anharmonicity of the bond potentials on the spectral density distributions. Therefore, for our present purposes, we make two simplifying assumptions:

- All moments, except for $\mu_q(h)$, are calculated in the harmonic oscillator basis. The results give good estimate of the exact values if the basis is sufficiently large, i.e. if $D_k \gg \omega_k$.
- In the final expressions χ_k are neglected relative to 1.

Then, using Eq. (68) we get

$$\mu_2(h_k) = \frac{1}{d_k} \sum_{n=0}^{d_k-1} (\varepsilon_n^k)^2 = \frac{4}{45} D_k^2(1 + O(\chi_k)) \quad (69)$$

and

$$\mu_3(h_k) = \frac{1}{d_k} \sum_{n=0}^{d_k-1} (\varepsilon_n^k)^3 = -\frac{16}{945} D_k^3(1 + O(\chi_k)). \quad (70)$$

Making use of the Eq. (27) and equations listed in the Appendix we obtain

$$\mu_{11}(h_k f_k) = -a_{11} \frac{(2D_k)^{3/2}}{\omega_k(m_k)^{1/2}}(1 + O(\chi_k)), \quad (71)$$

$$\mu_{12}(h_k f_k) = a_{12} \frac{D_k^2}{m_k \omega_k^2}(1 + O(\chi_k)), \quad (72)$$

where

$$a_{11} = \sum_{j=1}^{\infty} \frac{2^j - 2^{-j}}{j!(j+2)!} = 0.34003994 \dots, \quad (73)$$

and

$$a_{12} = 2 \sum_{j=1}^{\infty} \frac{(2j+1)(2^j - 2^{-j+1})}{j!(j+2)!} - \frac{1}{3} = 1.56428544 \dots \quad (74)$$

Finally, instead of Eq. (54) we have

$$\mu_2(f_k) = \frac{D_k}{m_k \omega_k^2} \left(1 + \frac{\omega_k}{4D_k}\right). \quad (75)$$

Then, in the case of bonds described by the Morse oscillators, Eqs. (21) and (22) become:

$$\begin{aligned} M_2 &= \frac{4}{45} \text{Tr}[\mathbf{D}^2 + \frac{45}{8}(\mathbf{\Lambda D})^2], \quad (76) \\ M_3 &= -\frac{16}{945} \text{Tr}(\mathbf{D}^3) + 24a_{11}^2 \sum_{kl}^N D_k^{3/2} \tilde{\Lambda}_{kl} D_l^{3/2} \\ &\quad + \text{Tr}[3a_{12} \tilde{\mathbf{\Lambda D}}^2 \tilde{\mathbf{\Lambda D}} + (\tilde{\mathbf{\Lambda D}})^3]. \quad (77) \end{aligned}$$

As one can see, the second moment expressions for the Morse and for the harmonic oscillator systems (Eqs. 76 and 56 respectively), are very similar. In the case of M_3 the first two terms in rhs of Eq. (77) (the Morse oscillators) do not have any counterparts in Eq. (57) (the harmonic oascillators). Particularly, the first of these terms may qualitatively influence the predicted shape of the spectrum.

If all D_k are the same and only the adjacent bond interactions described by a single coupling constant $\tilde{\lambda}$ are retained, then

$$M_2 = D^2 \left(\frac{4N}{45} + A_2 \tilde{\lambda}^2 \right), \quad (78)$$

$$M_3 = D^3 \left(-\frac{16N}{945} + 48a_{11}^2 A_2 \tilde{\lambda} + 6a_{12} A_2 \tilde{\lambda}^2 + 6 A_3 \tilde{\lambda}^3 \right). \quad (79)$$

In particular, for a ring molecule with $N > 3$ we have

$$M_3 = 9.3857 (N D^3) (\tilde{\lambda} + 0.5944)(\tilde{\lambda} - 0.003035), \quad (80)$$

for a linear molecule with three identical bonds

$$M_3 = 18.7713 D^3 (\tilde{\lambda} + 0.5959)(\tilde{\lambda} - 0.004541), \quad (81)$$

and for a three-member ring

$$M_3 = 6 D^3 (\tilde{\lambda} + 3.9983)(\tilde{\lambda} + 0.6976)(\tilde{\lambda} - 0.003035). \quad (82)$$

Let us note, that the skewness of the vibrational spectrum may be negative, zero, or positive depending on the value of $\tilde{\lambda}$ and on the molecular topology. In particular it is negative for small positive $\tilde{\lambda}$ (smaller than $3 \cdot 10^{-3} - 4 \cdot 10^{-3}$) and becomes positive for larger $\tilde{\lambda}$.

APPENDIX

Expressions for matrix elements of powers of the coordinate in the harmonic oscillator basis¹⁸ lead to simple formulas for moments. In particular, in the harmonic oscillator basis, Eq. (17) of Ref. 18 and the identity

$$\sum_{n=0}^{d-1} \binom{l+n}{l} = \binom{l+d}{l+1} \quad (83)$$

give

$$\mu_1(x^{2p}) = \frac{1}{d} \sum_{n=0}^{d-1} \langle n|x^{2p}|n \rangle \quad (84)$$

$$= \frac{1}{(m\omega)^p} \sum_{j=0}^p \frac{(d-1)!}{(d-j-1)!} A_{2p,j}, \quad (85)$$

where

$$A_{2p,j} = \frac{(2p)! 2^{j-2p}}{j!(p-j)!(j+1)!}. \quad (86)$$

Expanding in terms of powers of d we get

$$\begin{aligned} \mu_1(x^{2p}) &= \frac{A_{2p,p}}{(m\omega)^p} [(d-1)^p + p(d-1)^{p-1} \\ &+ \frac{p(p-1)(p+7)}{12}(d-1)^{p-2} + \dots + 2^{-p}(p+1)!]. \end{aligned} \quad (87)$$

Similarly,

$$\mu_1(e^{-\alpha x} x^{2p}) = \sum_{j=0}^{\infty} \frac{\alpha^{2j}}{(2j)!} \mu_1(x^{2(p+j)}), \quad (88)$$

$$\mu_1(e^{-\alpha x} x^{2p-1}) = - \sum_{j=0}^{\infty} \frac{\alpha^{2j+1}}{(2j+1)!} \mu_1(x^{2(p+j)}). \quad (89)$$

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- ¹⁴ The potentials describing interactions between bonds are unlimited neither from above nor from below. The total molecular potentials are limited from below in both harmonic oscillator and Morse cases and have minima at the equilibrium bond lengths, however they do not properly describe dissociation.
- ¹⁵ Let us note, that in this example the one-body Hamiltonian is equal to the harmonic oscillator one only in the limit of complete one-body space (i.e. $d \rightarrow \infty$). In the case under consideration $h' = \sum_{n=0}^{d-1} |n\rangle \varepsilon'_n \langle n|$, where $|n\rangle$ are eigenvectors of the harmonic oscillator Hamiltonian, cannot be represented in a simple way as a differential operator in the coordinate space.
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