THE THEORY OF THE ANHARMONIC OSCILLATOR

By K. S. Viswanathan, F.A.Sc.

(*Memoir No.* 97 *of the Raman Research Institute, Bangalore*-6)

Received May 22, 1957

1. Introduction

Anharmonicity of vibration plays an important role in several branches of physics. Its importance was first recognised in acoustics[1]; the presence of overtones of the fundamental mode of a tuning fork and the alteration of its pitch with intensity changes were successfully accounted for as the effects of the anharmonicity of the oscillator. More recently, the subject has acquired a fresh interest in relation to the subject of molecular spectroscopy.[2] The thermal expansion[3] of crystals also owes its origin to the anharmonic nature of the vibrations inside a crystal lattice.

It is the object of the present note to give an exact treatment of the classical problem of the anharmonic oscillator and also to draw attention to certain of its features which by an appeal to the Correspondence Principle lead to the results of wave mechanics. In Section 2, exact expressions have been given for the shift in the mean position of the oscillator from the origin, its frequency and the amplitudes of the different harmonics. In section 4, the eigenvalues of the oscillator are determined by using the W.K.B. method. It is shown that these are the solutions of a transcendental equation involving elliptic functions and that the first correction to any energy level of the system from its harmonic oscillator value is identical with the one obtained from the perturbation theory.

2. The Classical Problem

Let m denote the mass of the oscillator and x be its displacement. The potential energy of the system may be expressed as

$$V = \tfrac{1}{2}k_1x^2 + \frac{1}{3!}k_2x^3. \qquad (1)$$

We stop with the cubic term of the expansion since this is sufficient to explain most of the observed features of the spectra of diatomic molecules. Further, we take the constant k_2 to be negative in accordance with the conventions of molecular spectroscopy.

The equation of conservation of energy for the oscillator is

$$\tfrac{1}{2} m\dot{x}^2 + \tfrac{1}{2} k_1 x^2 + \tfrac{1}{6} k_2 x^3 = \bar{h} \tag{2}$$

where $\bar{h}$ is the energy of the system.

Or,

$$\frac{dx}{dt} = (A - \omega^2 x^2 + 4\alpha x^3)^{\frac{1}{2}} \tag{3}$$

where

$$A = \frac{2\bar{h}}{m}\,; \qquad \omega^2 = \frac{k_1}{m} \quad \text{and} \quad 4\alpha = -\frac{k_2}{3m}.$$

Before proceeding further, we consider the roots of the expression

$$f(x) = (4\alpha x^3 - \omega^2 x^2 + A) \tag{4}$$

which define the regions wherein the right-hand side of (3) is real. The discriminant of the cubic, namely $(G^2 + 4H^3)$, is equal to

$$64A\alpha^2\left(4A\alpha^2 - \frac{\omega^6}{27}\right)$$

and this will be negative as long as

$$\frac{A\alpha^2}{\omega^6} \angle \frac{1}{108}. \tag{5}$$

When this condition is satisfied all the three roots of $f(x) = 0$ are real, and two of them will be positive and the remaining one negative. Denoting these roots by x_1, x_2 and x_3 where $x_1 > x_2 > x_3$, we have

$$f(x) = 4\alpha\,(x - x_1)(x - x_2)(x - x_3). \tag{6}$$

Now $\{f(x)\}^{\frac{1}{2}}$ is real in two cases, *viz.*, (i) when $x > x_1$, or (ii) when x lies in the region $x_2 \geqslant x \geqslant x_3$.

For $x > x_1$,* the force acting on the molecule becomes repulsive and it increases with increasing distance of the oscillator from the origin. The vibrations in this case are unstable and the oscillator flies off to infinity within

---

* The solution in this case is given by $x = x_2 + (x_1 - x_2)\, nc^2\,(u, k)$. Since $cn\,(u, k)$ has zeros at points $u = (2n + 1)\,K$, where n is an integer, the displacement is infinite at these points. Thus within a period $t = \pi/\bar{\omega}$ after crossing the point x_1, the molecule dissociates.

a short period after crossing the point x_1. In other words, when the internuclear distance of a diatomic molecule exceeds its equilibrium value by an amount x_1, the molecule will dissociate.

The vibrations in the region $x_2 \geqslant x \geqslant x_3$ are stable and retain in a measure the characteristics of a harmonic oscillator. Writing

$$\tau = \frac{A^{\frac{1}{2}}\alpha}{\omega^3},$$

the roots of $f(x) = 0$ are approximately

$$x_1 = \frac{\omega^2}{4\alpha}(1 - 16\tau^2 - 512\tau^4)$$

$$x_2 = \frac{\sqrt{A}}{\omega}(1 + 2\tau + 10\tau^2 + 64\tau^3 + 224\tau^4)$$

$$x_3 = -\frac{\sqrt{A}}{\omega}(1 - 2\tau + 10\tau^2 - 64\tau^3 + 224\tau^4). \tag{7}$$

The above relations were derived by using the bionomial expansion in the expressions for the roots of the cubic, assuming that τ is small. One can however easily verify by substitution that they satisfy the equation $f(x) = 0$ upto terms of the order of ω^{-9}. Equation (3) can now be written as

$$t = \frac{1}{2\sqrt{\alpha}} \int_{x_3}^{x} \frac{dx}{\{(x - x_1)(x - x_2)(x - x_3)\}^{\frac{1}{2}}}. \tag{8}$$

The right-hand side of the above equation is an elliptic integral and its value[4] is

$$\frac{1}{2\sqrt{\alpha}} \times \frac{2}{\sqrt{x_1 - x_3}}\, sn^{-1}\left(\sqrt{\frac{x - x_3}{x_2 - x_3}},\ \sqrt{\frac{x_2 - x_3}{x_1 - x_3}}\right).$$

Hence writing $u = \sqrt{\alpha(x_1 - x_3)}\, t$ and

$$k^2 = \frac{(x_2 - x_3)}{(x_1 - x_3)},$$

we get the wellknown solution

$$x = x_3 + (x_2 - x_3)\, sn^2(u, k). \tag{9}$$

Given the energy of the oscillator, the above equation determines its complete course in time.

In view of their periodicity properties, the Jacobian elliptic functions admit of expansions as Fourier series. For the function $sn^2(u, k)$, we have the following expansion[5] (see Whittaker and Watson, p. 520, example 5):

$$sn^2(u, k) = \left(\frac{\pi}{k\mathrm{K}}\right)^2 \left\{\frac{\mathrm{K}(\mathrm{K}-\mathrm{E})}{\pi^2} - 2\sum_{n=1}^{\infty} \frac{nq^n}{(1-q^{2n})}\cos 2ny\right\} \tag{10}$$

where

$$y = \frac{\pi}{2\mathrm{K}}u; \tag{11}$$

K and E are the complete elliptic integrals of the first and second type which in terms of hyper-geometric functions are defined by

$$\mathrm{K} = \frac{\pi}{2}\mathrm{F}\left(\tfrac{1}{2}, \tfrac{1}{2}, 1;\ k^2\right)$$

$$\mathrm{E} = \frac{\pi}{2}\mathrm{F}\left(-\tfrac{1}{2}, \tfrac{1}{2}, 1;\ k^2\right) \tag{12}$$

and q is a parameter which is related to the modulus k of the elliptic function by means of the formula

$$q = \epsilon + 2\epsilon^5 + 15\epsilon^9 + 150\epsilon^{13} + 0(\epsilon^{17}) \tag{13}$$

where again

$$2\epsilon = \frac{1-\sqrt{k^1}}{1+\sqrt{k^1}}$$

and

$$k^1 = (1-k^2)^{\frac{1}{2}}.$$

Substituting (10) in (9) we get

$$x = x_3 + \frac{(x_2 - x_3)}{(\mathrm{K}k)^2}\left[\mathrm{K}(\mathrm{K}-\mathrm{E}) - 2\pi^2 \sum_{n=1}^{\infty} \frac{nq^n}{(1-q^{2n})}\cos 2ny\right]. \tag{14}$$

Equation (14) shows that the displacement of the oscillator is no longer a simple sinusoidal function, but contains a constant term and harmonics of the fundamental mode. The coefficient of t in $2y$ namely $(\pi/\mathrm{K})\sqrt{\alpha(x_1 - x_3)}$

gives the circular frequency of the system. Denoting this by $\tilde{\omega}$, we have therefore

$$\tilde{\omega} = \frac{\pi}{\mathrm{K}} \sqrt{\alpha (x_1 - x_3)} \tag{15}$$

The shift $\langle x \rangle$ in the mean position of the oscillator is given by the constant term of the expansion (14) and is equal to

$$x_3 + \frac{(x_2 - x_3)(\mathrm{K} - \mathrm{E})}{\mathrm{K}k^2} \tag{16}$$

The amplitude of the nth harmonic is proportional to

$$\frac{nq^n}{(1 - q^{2n})}. \tag{17}$$

In particular the intensities of the first three harmonics are in the ratio

$$\frac{q^2}{(1 - q^2)^2} : \frac{4q^4}{(1 - q^4)^2} : \frac{9q^6}{(1 - q^6)^2}. \tag{17a}$$

Equations (15) and (16) express the frequency of the oscillator and its mean shift as functions involving elliptic integrals. We shall now obtain approximations for these which are useful for appreciating their physical magnitudes as well as for comparison with earlier work.

The following expansions now hold good for k^2, K, (K − E) and $\sqrt{\alpha (x_1 - x_3)}$ when $\tau \ll 1$:

$$\begin{aligned} k^2 &= 8\tau (1 - 4\tau + 50\tau^2 - 336\tau^3 + 3694\tau^4) \\ \mathrm{K} &= \frac{\pi}{2}(1 + 2\tau + \tau^2 + 78\tau^3) \\ \sqrt{\alpha (x_1 - x_3)} &= \frac{\omega}{2}(1 + 2\tau - 14\tau^2 + 48\tau^3) \\ (\mathrm{K} - \mathrm{E}) &= 2\pi\tau (1 - \tau + 41\tau^2 - 80{\cdot}5\tau^3). \end{aligned} \tag{18}$$

Substituting (7) and (18) in (15) and (16), one finds after some simplification that the change in frequency of the oscillator and its mean displacement from the origin are approximately given by

$$(\tilde{\omega} - \omega) = \frac{-15\mathrm{A}\alpha^2}{\omega^5} \tag{19}$$

$$\langle x \rangle = \frac{3\mathrm{A}\alpha}{\omega^4} + \frac{225}{2} \frac{\mathrm{A}^2\alpha^3}{\omega^{10}} \tag{20}$$

respectively. The reader can easily see these to be the same as the expressions given in books on acoustics.

3. SOME REMARKS

We shall now consider how the frequency and mean shift of the oscillator get modified when the energy of the system is altered. Remembering that the quantity A occurring in equations (19, 20) is a constant multiple $(2/m)$ of the energy $\bar{h}$ of the system, we get on differentiation of (19) with respect to $\bar{h}$ that

$$\frac{d\tilde{\nu}}{d\bar{h}} = \frac{-15a^2}{\pi m\omega^5} \tag{21}$$

where

$$\tilde{\nu} = \frac{\tilde{\omega}}{2\pi}.$$

Thus to an approximation which ignores terms of the order of τ^4, we see that the frequency of the oscillator is a decreasing function of the energy, the rate of decrease being a constant characteristic of the oscillator.

From (21) it follows that the change in the frequency of the system as its energy is increased from ϵ_1 to ϵ_2 is

$$\frac{-15a^2}{\pi m\omega^5}(\epsilon_2 - \epsilon_1).$$

Writing $\epsilon_2 = (v + 3/2)\,h\nu$ and $\epsilon_1 = (v + \frac{1}{2})\,h\nu$, we see that this is equal to

$$\frac{-15a^2}{\pi m\omega^5}\,h\nu$$

or

$$\frac{-5}{48}\,\frac{k_2{}^2 h\nu}{\pi\,(mk_1{}^5)^{\frac{1}{2}}}$$

which is the value given by the perturbation theory.[6] Hence in this case even a semi-classical theory is able to give the correct results yielded by wave-mechanics.

Differentiating now (20) with respect to $\bar{h}$, one finds that

$$\frac{d\langle x\rangle}{d\bar{h}} = \frac{6a}{m\omega^4} + \frac{900a^3}{(m\omega^5)^2}\,\bar{h} \tag{22}$$

which shows that the mean shift of the oscillator increases with rise in the energy of the system.

As before, the magnitude of the shift in the *v*th state may be obtained by writing $\epsilon_v = (v + \frac{1}{2})\, h\nu$ in (20). We have

$$\langle x \rangle_v = \frac{3ah}{\pi m \omega^3} (v + \tfrac{1}{2}) + \frac{225}{2} \frac{h^2 a^3}{\pi^2 m^2 \omega^8} (v + \tfrac{1}{2})^2. \tag{23}$$

From the above, it is possible to obtain the stretch (or contraction) in the bond-length of a diatomic molecule during a transition between two different quantum states specified by the numbers v and v' respectively. This is given by

$$\frac{3ah}{\pi m \omega^3} (v' - v) + \frac{225}{2} \frac{h^2 a^3}{\pi^2 m^2 \omega^8} (v' - v)(v' + v + 1) \tag{24}$$

4. THE ENERGY LEVELS

The Schrodinger equation for the oscillator is given by

$$\frac{d^2 u}{dx^2} + \frac{8\pi^2 m}{h^2} (\epsilon - \mathrm{V})\, u = 0 \tag{25}$$

where V has the form given in (1). A method for determining the eigenvalues of an equation of the above type was developed by Wentzel, Kramers and Brillouin, and this was later refined by Langer.[7] According to the latter, if x_3 and x_2 are two consecutive simple zeroes of $\epsilon - \mathrm{V}(x)$ such that $\epsilon > \mathrm{V}$ for $x > x_3$, and $\epsilon < \mathrm{V}$ for $x > x_2$, the eigenvalues of (25) are determined by

$$(n + \tfrac{1}{2})\, \pi = \int_{x_3}^{x_2} \left\{ \frac{8\pi^2 m}{h^2} (\epsilon - \mathrm{V}) \right\}^{\frac{1}{2}} dx. \tag{26}$$

Writing $\mathrm{A} = 2\epsilon/m$, the above equation becomes

$$(n + \tfrac{1}{2})\, \pi = \frac{2\pi m}{h}\, \mathrm{I} \tag{27}$$

where

$$\mathrm{I} = \int_{x_3}^{x_2} (4ax^3 - \omega^2 x^2 + \mathrm{A})^{\frac{1}{2}}\, dx.$$

The integral I has been evaluated in Appendix I and substituting the value given for it there in (27), one gets

$$(n + \tfrac{1}{2})\, h = \frac{8m}{15} \sqrt{a\eta_2}\, \{ -(\mathrm{K} - \mathrm{E})\, [\Sigma (x_2 - x_3)^2] + \eta_1 (\eta_1 + \eta_2)\, \mathrm{K} \} \tag{28}$$

where $\eta_1 = (x_2 - x_3)$ and $\eta_2 = (x_1 - x_3)$, The quantities occurring on the right-hand side of the above equation are all functions of ϵ and hence by solving this transcendental equation for different integral values of n, the eigenvalues $\epsilon_1, \epsilon_2, \ldots\ldots\ldots \epsilon_n$ of the oscillator may be determined.

In practice, equation (28) can be solved by expressing the right-hand side as a power series in the parameter τ which will result in a series expansion in ϵ and then inverting the series. For example, by making use of the expansions (7) and (18) and further of the following relations

$$\Sigma (x_2 - x_3)^2 = \frac{\omega^4}{8a^2}; \tag{29}$$

$$\eta_1 (\eta_1 + \eta_2) = \frac{\sqrt{A}\omega}{2a} (1 + 12\tau - 14\tau^2 + 240\tau^3)$$

it can be seen that (28) is equivalent to

$$(n + \tfrac{1}{2})\, h = 2m \cdot \frac{\pi A}{2\omega} \left(1 + \frac{15}{2}\tau^2 + 0(\tau^4)\right). \tag{30}$$

Or, writing $a = - k_2/12m$, $\omega = 2\pi\nu$ and $A = 2\epsilon/m$ we have

$$(n + \tfrac{1}{2})\, h\nu = \epsilon + \frac{5}{96\pi\nu} \frac{k_2{}^2}{(mk_1{}^5)^{\frac{1}{2}}} \epsilon^2.$$

Hence

$$\epsilon = (n + \tfrac{1}{2})\, h\nu - \frac{5}{96} \frac{k_2{}^2 h^2 \nu}{\pi (mk_1{}^5)^{\frac{1}{2}}} (n + \tfrac{1}{2})^2 \tag{31}$$

which is the eigenvalue of the oscillator as obtained from the perturbation theory correct to the second order. By expanding (25) still further than in (27), one can obtain higher order corrections.

The author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in this work.

SUMMARY

Exact expressions have been obtained for the frequency of an anharmonic oscillator, the shift in its equilibrium position from the origin and for the amplitudes of its different harmonics. It is shown that the frequency of the oscillator is a decreasing function of the energy and that some of the results of wave-mechanics can be obtained from the classical theory by substituting in the classical energy of the oscillator the different energy values of a harmonic oscillator. The eigenvalues of the oscillator are determined by using the W.K.B. method. The classical theory of a Morse oscillator has similarly been worked out in Appendix II.

REFERENCES

1. Lord Rayleigh .. *Theory of Sound*, 1948, pp. 76–78.
2. Herzberg, G. .. *Spectra of Diatomic Molecules*, Second Edition, pp. 90–102.
3. Fermi, E. .. *Moleküle und Kristalle*, p. 140.
4. Magnus, W. and Oberhettinger *Formulas and Theorems for the Special Functions of Mathematical Physics*, 1949, 108.
5. Whittaker and Watson .. *Modern Analysis*, Fourth Edition (Chapters XXI and XXII).
6. Ta-You-Wu .. *Vibrational Spectra and Structure of Polyatomic Molecules*, 1939, 48.
7. Langer, R. E. .. *Phys. Rev.*, 1937, **51**, 669.
8. Morse, P. M. .. *Ibid.*, 1929, **34**, 57.

APPENDIX 1

Evaluation of the integral $\mathrm{I} = \int_{x_3}^{x_2} \sqrt{4ax^3 - \omega^2 x^2 + \mathrm{A}}\, dx$.

Obviously we have

$$\mathrm{I} = \int_{x_3}^{x_2} \frac{(4ax^3 - \omega^2 x^2 + \mathrm{A})}{2\sqrt{a}\,\{(x - x_1)(x - x_2)(x - x_3)\}^{\frac{1}{2}}}\, dx. \tag{1}$$

If we substitute $(x - x_3) = y^2$ in the above equation and denote by Q_m the integral

$$\int_0^{\sqrt{\eta_1}} \frac{x^m dx}{\sqrt{(x^2 - \eta_1)\ (x^2 - \eta_2)}}$$

where $\eta_1 = (x_2 - x_3)$ and $\eta_2 = (x_1 - x_3)$, equation (1) takes the form

$$\mathrm{I} = (p\mathrm{Q}_6 + q\mathrm{Q}_4 + r\mathrm{Q}_2 + s\mathrm{Q}_0) \tag{2}$$

where

$$p = 4\sqrt{a}\ ;$$

$$q = \sqrt{a}\left(12x_3 - \frac{\omega^2}{a}\right);$$

$$r = \sqrt{a}\left(12x_3^2 - \frac{2\omega^2 x_3}{a}\right);\quad \text{and}$$

$$s = \frac{1}{\sqrt{a}}(4ax_3^3 - \omega^2 x_3^2 + \mathrm{A}).$$

Since x_3 is a root of $f(x) = 0$, the constant s in the above is equal to zero.

The integrals Q_m can be evaluated by reduction formulæ. For example,

$$\frac{d}{dx}\{x^3\sqrt{\mathrm{Q}}\} = \frac{3x^2\mathrm{Q}}{\sqrt{\mathrm{Q}}} + \frac{x^3\mathrm{Q}'}{2\sqrt{\mathrm{Q}}}$$

where

$$\mathrm{Q} = \sqrt{(x^2 - \eta_1)\ (x^2 - \eta_2)}.$$

If we integrate this equation between 0 and $\eta_1^{\frac{1}{2}}$, the left-hand side vanishes and we get

$$\mathrm{Q}_6 = \frac{1}{5}(4a\mathrm{Q}_4 - 3b\mathrm{Q}_2) \tag{3}$$

where

$$a = (\eta_1 + \eta_2) \qquad \text{and} \qquad b = \eta_1 \eta_2.$$

Similarly

$$Q_4 = \tfrac{1}{3}(2aQ_2 - bQ_0). \tag{4}$$

Substituting (3) and (4) in (2) we get after some reduction that

$$I = -\frac{4}{15}\sqrt{a}\,\{2Q_2(x_1^2 + x_2^2 + x_3^2) - abQ_0\}. \tag{5}$$

Now

$$Q_0 = \int_0^{\sqrt{\eta_1}} \frac{dx}{\sqrt{Q}} = \frac{K}{\sqrt{\eta_2}}. \tag{6}$$

Next by the substitution $x = z\sqrt{\eta_1}$, we find that

$$Q_2 = \frac{\eta_1}{\sqrt{\eta_2}} \int_0^1 \frac{z^2 dz}{\{(1 - z^2)(1 - k^2 z^2)\}^{\frac{1}{2}}}$$

where

$$k^2 = \frac{\eta_1}{\eta_2}$$

$$\text{Or } Q_2 = \frac{\eta_1}{\sqrt{\eta_2}} \int_0^K sn^2(u, k)\, du = \sqrt{\eta_2}\,(K - E). \tag{7}$$

Substituting (6) and (7) in (5), one gets

$$I = \frac{4}{15}\sqrt{a\eta_2}\,\{-\Sigma(x_2 - x_3)^2 (K - E) + \eta_1(\eta_1 + \eta_2) K\} \tag{8}$$

APPENDIX II

The potential (1, Section 2) is valid, when the vibrations are small but nevertheless depart from harmonicity. Apart from its applications in acoustics, it is useful in studying anharmonicity in complex molecules when one splits their vibrations into those of an assembly of anharmonic oscillators. For diatomic molecules however Morse[8] suggested a potential given by

$$\mathrm{V} = \mathrm{D}\,(1 - e^{-\beta x})^2 \tag{1}$$

where D is the dissociation energy of the molecule and β is a constant, which holds good approximately upto the dissociation range. The quantum mechanical energy values of an oscillator moving in a potential field of the type (1) was given by Morse. We give below the classical theory of such an oscillator which merits attention in view of its extreme simplicity and for purposes of comparison with the quantum theory.

The equation of energy for the Morse oscillator is

$$\tfrac{1}{2}\, m\dot{x}^2 + \mathrm{D}\,(1 - e^{-\beta x})^2 = \bar{h} \tag{2}$$

where as before $\bar{h}$ denotes the energy of the system. Hence

$$\dot{x}^2 = c + by + ay^2 \tag{3}$$

where

$$c = \frac{2}{m}(\bar{h} - \mathrm{D})\,; \quad b = \frac{4\mathrm{D}}{m}\,; \quad a = \frac{-2\mathrm{D}}{m}$$

and

$$y = e^{-\beta x}. \tag{4}$$

c can immediately be seen to be negative.

The turning points for the oscillator in its course are $-1/\beta \log\,(1 + \sqrt{h/\mathrm{D}})$ and $-1/\beta \log.\,(1 - \sqrt{h/\mathrm{D}})$. We shall measure time from the instant the oscillator is at its extremity in the left.

From (3) and (4) we get

$$t = -\frac{1}{\beta}\int \frac{dy}{y\sqrt{ay^2 + by + c}} \tag{5}$$

or

$$\beta t = \frac{1}{\sqrt{-c}}\,\cos^{-1}\frac{by + 2c}{y\sqrt{b^2 - 4ac}}. \tag{6}$$

Hence we have

$$x = \frac{1}{\beta} \log \frac{\mathrm{D}}{(\mathrm{D} - \bar{h})} + \frac{1}{\beta} \log \left\{ 1 - \sqrt{\frac{\bar{h}}{\mathrm{D}}} \cos \beta t \sqrt{\frac{2}{m} (\mathrm{D} - \bar{h})} \right\} \tag{7}$$

The above equation determines the course of the oscillator with time.

From (7) it is immediately obvious that the frequency of the gravest mode is given by

$$\tilde{\nu} = \frac{\beta}{2\pi} \sqrt{\frac{2}{m}} (\mathrm{D} - \bar{h}) \tag{8 a}$$

$$= \nu \left(1 - \frac{\bar{h}}{\mathrm{D}}\right)^{\frac{1}{2}} \tag{8 b}$$

where

$$\nu = \frac{\beta}{2\pi} \sqrt{\frac{2\mathrm{D}}{m}};$$

ν will be the (harmonic oscillator) frequency of the system when the anharmonic terms in the expansion of (1) as a power series in x are neglected.

The eigenvalues of a Morse oscillator are

$$\mathrm{E}_n = (n + \tfrac{1}{2}) h\nu - z (n + \tfrac{1}{2})^2 h\nu \tag{9}$$

where

$$z = \frac{\beta^2 h}{8\pi^2 m \nu} = \frac{h\nu}{4\mathrm{D}}. \tag{10}$$

The frequency of emission of the oscillator during a transition from the nth state to the one immediately below it is given by

$$\begin{aligned} \nu_{n,\, n-1} = \nu_n^{em} &= \nu (1 - 2nz) \\ &= \nu \left\{ z + \sqrt{\frac{1 - 4z\mathrm{E}_n}{h\nu}} \right\} \\ &= \nu \left\{ z + \sqrt{1 - \frac{\mathrm{E}_n}{\mathrm{D}}} \right\} \end{aligned} \tag{11 a}$$

from (10).

Similarly the frequency of absorption from the nth state is given by

$$\nu_n^{ab} = \nu_{n+1,\, n} = \nu \left\{ - z + \sqrt{1 - \frac{\mathrm{E}_n}{\mathrm{D}}} \right\}. \tag{11 b}$$

Equation (8 b) shows that the frequency of the classical oscillator is a decreasing function of its energy. The dependence of the frequencies of emission or absorption on the transitional energy levels is likewise described by (11 *a*) and (11 *b*). Apart from the first term which is a consequence of the quantum phenonmenon that has no classical analogue, namely, that the molecule possesses a zero-point energy and on the non-linear dependence of the energy levels on the quantum numbers, the formulæ (11) possess a striking resemblance to the classical formula (8 *b*). In fact $(\nu_n{}^{ab} + \nu_n{}^{em})/2$ depends on the energy of the *n*th level in the same way as the classical frequency does with the energy of the system. When the energy equals its dissociation value the discrete spectrum stops for the oscillator.[8] Classically its frequency then vanishes.

In order to find out the shift in the mean position of the oscillator and the amplitudes of the different harmonics, we express x as a Fourier cosine series in the form

$$x = a_0 + \sum_{n=1}^{\infty} a_n \cos nu \tag{12}$$

where $u = 2\pi\, \tilde{\nu} t$. Then

$$\begin{aligned} a_0 &= \frac{1}{\beta}\log \frac{\mathrm{D}}{(\mathrm{D}-\bar{h})} + \frac{1}{2\pi\beta}\int_{-\pi}^{+\pi} \log\left(1 - \sqrt{\frac{\bar{h}}{\mathrm{D}}}\cos u\right) du \\ &= \frac{1}{\beta}\log \frac{\mathrm{D}}{(\mathrm{D}-\bar{h})} + \frac{1}{\beta}\log \tfrac{1}{2}\left\{1 + \sqrt{1 - \frac{\bar{h}}{\mathrm{D}}}\right\} \\ &= \frac{1}{\beta}\log \tfrac{1}{2}\left\{\frac{1 + \sqrt{1 - \frac{\bar{h}}{\mathrm{D}}}}{1 - \frac{\bar{h}}{\mathrm{D}}}\right\}. \end{aligned} \tag{13}$$

From the above it follows that the shift in the mean position of the oscillator increases with the energy of the system and tends logarithmically to infinity when the energy approaches its dissociation value.

Next we have

$$a_n = \frac{1}{\pi\beta}\int_{-\pi}^{\pi} \log\left(1 - \sqrt{\frac{\bar{h}}{\mathrm{D}}}\cos u\right) \cos nu\; du. \tag{14}$$

The integral may be evaluated by expanding the logarithmic function as a power series, and integrating term by term the resulting series which can be seen to be uniformly convergent for all values of u in $(-\pi, \pi)$. Thus one gets

$$a_n = -\frac{1}{\beta}\sum_{s=n/2}^{\infty}\left(\frac{\bar{h}}{\mathrm{D}}\right)^{s}\frac{1}{2s2^{2s-1}}\begin{pmatrix}2s\\ \frac{2s-n}{2}\end{pmatrix} \tag{15 a}$$

for even values of *n* and

$$a_n = -\frac{1}{\beta}\sum_{s=n-1/2}^{\infty}\left(\frac{\bar{h}}{\mathrm{D}}\right)^{2s+1/2}\frac{1}{(2s+1)\,2^{2s}}\begin{pmatrix}2s+1\\ \frac{2s+1-n}{2}\end{pmatrix} \tag{15 b}$$

for odd values of *n*.

The above formulæ give the law of dependence of the amplitudes of the various harmonics on the energy of the oscillator. One notices that the amplitude of the *n*th harmonic is of the order of $(\bar{h}/\mathrm{D})^{n/2}$.