Some Properties of a Quartic Potential with a Finite Binding Energy

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A potential energy function is proposed which exhibits a quartic dependence on $(r - r_e)$, where r_e is the equilibrium interparticle distance, in the neighbourhood of r_e, and has a finite binding energy. To study the pattern of the eigenvalues, the WKBJ method is applied to the third order, and the relevant integrals are evaluated analytically. Results are shown graphically for a few sets of parameters. The number of vibrational states that the potential can support is determined for a range of values of the parameters. Some suggestions as to the possible applications of the proposed potential are also made.

1. Introduction

In nature, there are four types of forces acting:

1. The gravitational interactions.
2. The electromagnetic interactions.
3. The strong nuclear interactions.
4. The weak interactions.

While the exact analytical forms for the potential in the first two cases are known, this is not the case for the last two.

The basic potential governing all electromagnetic interactions is the Coulomb potential. However, when we impose the rules of quantum mechanics on it, we get various secondary effective potentials, the shape of many of which, if there is a bound state, is of the type as the broken-line curve shown in Figure 1. The effective potentials between two atoms or between two molecules are often of this type [1, 2]. The effective potential experienced by a valence electron in an atom can also be represented by such a shape. The leading term in such interactions is usually of a harmonic oscillator type,

$$V(x) = A\,x^2\,. \tag{1}$$

If one is considering two particles, $x = r - r_e$, where r_e is the equilibrium interparticle distance. The harmonic oscillator potential is encountered in many areas of physics.

Another potential that occurs in certain areas of physics, is the quartic potential

$$V(x) = a\,x^4\,. \tag{2}$$

Bell [3] first pointed out in 1945 that there may be some types of molecular vibration for which a potential of the form (2) may be applicable. He calculated the first few eigenvalues for this potential. Kilpatrick and Kilpatrick [4] obtained accurate eigenvalues for levels up to and including $n = 16$.

The mixed quartic-harmonic oscillator,

$$V(x) = A\,(x^4 + B\,x^2)\,, \tag{3}$$

was first investigated in detail by McWeeny and Coulson [5] who derived approximate formulas for the energy levels.

During the sixties, it was found [6–8] that a good many ring compounds exhibit ring-puckering vibrations which can be described by one of the potentials (2) or (3). In this context, x is the ring-puckering coordinate. The eigenvalues for the quartic and the mixed quartic-harmonic oscillator have been calculated by a number of workers [9–16]. The quartic potential has also been investigated by Heisenberg [17], Yamazaki [18], and by Titchmarsh [19] in different contexts.

Secrest et al. [9] and Krieger et al. [20] have studied general potentials of the type

$$V(x) = a\,x^{2\nu}\,, \tag{4}$$

where ν is an integer.

The potentials (1) and (2) represent an idealized situation, the two particles interacting via either of these remain bound for all finite values of the energy. In actual physical systems, however, the two particles will dissociate beyond a certain energy. A good number of potentials are available [1, 2] which exhibit this property, and for small

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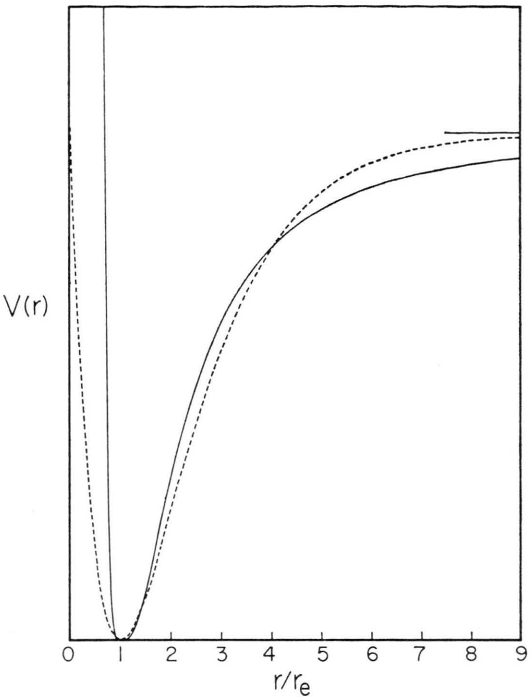

Fig. 1. Comparison of the potential (5) (solid-line curve) with the Morse potential (broken-line curve). The constant m was given a value 2.

values of x, show the harmonic oscillator type of dependence on x.

In this paper we suggest an interesting potential which, for small values of x, shows a quartic dependence of the form (2), and has a finite binding energy. We investigate the energy eigenvalues for this potential by the third-order WKBJ approximation and also determine the number of vibrational levels that it can support. Some suggestions as to its possible applications are also made.

2. A New Potential

The proposed potential is as follows:

$$V(r) = D[\{(r_e/r)^m - 1\}^4 - 1]\,, \tag{5}$$

where D is the well depth, and r_e is the equilibrium interparticle distance; m is a constant, which, for convenience, may be taken to be an integer. The potential (5) has the interesting property that its first three derivatives all vanish at $r = r_e$. The quartic term in the Taylor expansion makes the dominant contribution in the neighbourhood of $r = r_e$; the higher-order terms are, of course, present. The shape of the potential for $m = 2$ is shown by the full-line curve in Figure 1. The broken-line curve shown in Fig. 1 is actually the Morse potential, with the parameters chosen such that the well depths and the values of the two potentials at $r = 4r_e$ are the same. (The choice $r = 4r_e$ is arbitrary.) We notice that the potential (5) has a much "harder" core than the Morse potential.

The Schrödinger equation for the potential (5) is not solvable analytically. However, we have found it possible to evaluate analytically the relevant integrals up to the third-order in the WKBJ approximation, and thus have been able to calculate the energy eigenvalues.

3. Application of the Third-Order WKBJ Approximation

In the WKBJ method, the quantization condition to the third-order in $\hbar^2$ can be expressed [21] as

$$\begin{aligned}(n+\tfrac{1}{2})\frac{h}{\sqrt{2\mu}} &= \oint_c (E-V)^{1/2}\,\mathrm{d}x \\ &\quad - \frac{\hbar^2}{64\mu}\oint_c V'^2(E-V)^{-5/2}\,\mathrm{d}x \\ &\quad - \frac{\hbar^4}{8192\mu^2}\oint_c [49\,V'^4(E-V)^{-11/2} \\ &\quad - 16\,V'\,V'''(E-V)^{-7/2}]\,\mathrm{d}x\,.\end{aligned} \tag{6}$$

Here the domain of x is the complex plane cut along the real axis between the classical turning points and the integration is carried along a contour c enclosing the classical turning points but no other singularities of the integrands, and not crossing the cut.

Whereas integration of the first-order term does not present much difficulty, evaluation of higher-order terms in (6) is difficult because the integrands have nonintegrable singularities at the classical turning points. However, Krieger et al. [20] have transformed the second and third-order terms, by repeated integrations by parts, to simple expressions, and (6) may be rewritten as

$$\begin{aligned}(n+\tfrac{1}{2})\frac{h}{\sqrt{2\mu}} &= \oint_c (E-V)^{1/2}\,\mathrm{d}x \\ &\quad - \frac{\hbar^2}{48\mu}\frac{\mathrm{d}}{\mathrm{d}E}\oint_c V''(E-V)^{-1/2}\,\mathrm{d}x \\ &\quad + \frac{\hbar^4}{11520\mu^2}\frac{\mathrm{d}^3}{\mathrm{d}E^3} \\ &\quad \oint_c (7\,V''^2 - 5\,V'\,V''')(E-V)^{-1/2}\,\mathrm{d}x\,.\end{aligned} \tag{7}$$

The integrands in (7) are now free of nonintegrable singularities and we evaluate the integrals by taking twice the integrand and integrating along the real axis from one turning point to another. Thus

$$(n+\tfrac{1}{2})\frac{\hbar}{\sqrt{2\mu}}=\int_{r_1}^{r_2}2(E-V)^{1/2}\,\mathrm{d}r -\frac{\hbar^2}{24\mu}\frac{\mathrm{d}}{\mathrm{d}E}\int_{r_1}^{r_2}\frac{V''}{(E-V)^{1/2}}\,\mathrm{d}r +\frac{\hbar^4}{5760\mu^2}\times\frac{\mathrm{d}^3}{\mathrm{d}E^3}\int_{r_1}^{r_2}\frac{7V''^2-5V'V'''}{(E-V)^{1/2}}\,\mathrm{d}r\,, \tag{8}$$

where r_1 and r_2 are, respectively, the smaller and larger positive roots of $E-V(r)=0$.

Let us rewrite (8) as

$$n+\tfrac{1}{2}=I_1+I_2+I_3\,, \tag{9}$$

where I_1, I_2, and I_3 are respectively the first, second and the third terms of the right hand side of (8) each multiplied by $\sqrt{2\mu}/\hbar$. Thus

$$I_1=\frac{2\sqrt{2\mu}}{\hbar}\int_{r_1}^{r_2}(E-D[\{(r_\mathrm{e}/r)^m-1\}^4-1])^{1/2}\,\mathrm{d}r\,. \tag{10}$$

On substituting

$$(r_\mathrm{e}/r)^m=1+\omega\,, \tag{11}$$

and setting

$$(1+E/D)^{1/4}=\omega_0\,,$$

we obtain

$$\begin{aligned}I_1&=\frac{2r_\mathrm{e}\sqrt{2\mu D}}{m\hbar}\int_{-\omega_0}^{\omega_0}(\omega_0^4-\omega^4)^{1/2}(1+\omega)^{-1-1/m}\,\mathrm{d}\omega\\&=\frac{2\eta}{\pi m}\int_0^{\omega_0}(\omega_0^4-\omega^4)^{1/2}\times[(1+\omega)^{-1-1/m}+(1-\omega)^{-1-1/m}]\,\mathrm{d}\omega\,,\end{aligned} \tag{12}$$

where

$$\eta=\pi r_\mathrm{e}\sqrt{2\mu D}/\hbar\,.$$

By the binomial theorem [22], we write

$$\begin{aligned}&(1+\omega)^{-1-1/m}+(1-\omega)^{-1-1/m}\\&=\sum_{k=0}^{\infty}\frac{(1+1/m)_k}{k!}\{(-1)^k+1\}\,\omega^k\,,\quad|\omega|<1\,.\\&=2\sum_{k=0}^{\infty}\frac{(1+1/m)_{2k}}{(2k)!}\,\omega^{2k}\,.\end{aligned} \tag{13}$$

Substituting this in (12) and reversing the order of integration and summation which is justified provided $|\omega_0|<1$, we obtain

$$I_1=\frac{4\eta}{\pi m}\sum_{k=0}^{\infty}\frac{(1+1/m)_{2k}}{(2k)!}\int_0^{\omega_0}(\omega_0^4-\omega^4)^{1/2}\,\omega^{2k}\,\mathrm{d}\omega$$

which can be evaluated to give

$$I_1=\frac{\eta\,\omega_0^3}{2\sqrt{\pi}\,m}\sum_{k=0}^{\infty}\frac{\Gamma(1+1/m+2k)\,\Gamma(k/2+1/4)}{\Gamma(1+1/m)\,\Gamma(1+2k)\,\Gamma(k/2+7/4)}\,\omega_0^{2k},\quad|\omega_0|<1\,. \tag{14}$$

Collecting the odd and even powers of ω_0^2 separately, we rewrite I_1 as

$$I_1=\frac{\eta}{2\sqrt{\pi}\,m\,\Gamma(1+1/m)}\left[\omega_0^3\sum_{k=0}^{\infty}\frac{\Gamma(1+1/m+4k)\,\Gamma(k+1/4)}{\Gamma(1+4k)\,\Gamma(k+7/4)}(\omega_0^4)^k+\omega_0^5\sum_{k=0}^{\infty}\frac{\Gamma(3+1/m+4k)\,\Gamma(k+3/4)}{\Gamma(3+4k)\,\Gamma(k+9/4)}(\omega_0^4)^k\right]$$

which expressed in terms of hypergeometric functions [22] is

$$\begin{aligned}I_1=\frac{\eta}{m\sqrt{\pi}}\Bigg[&\frac{2g}{3}\,\omega_0^3\;{}_4F_3\left\{\frac{1}{4}+\frac{1}{4m},\frac{1}{2}+\frac{1}{4m},\frac{3}{4}+\frac{1}{4m},1+\frac{1}{4m};\frac{1}{2},\frac{3}{4},\frac{7}{4};\omega_0^4\right\}\\&+\frac{4}{5g}(2+1/m)(1+1/m)\,\omega_0^5\;{}_4F_3\left\{\frac{3}{4}+\frac{1}{4m},1+\frac{1}{4m},\frac{5}{4}+\frac{1}{4m},\frac{3}{2}+\frac{1}{4m};\frac{5}{4},\frac{3}{2},\frac{9}{4};\omega_0^4\right\}\Bigg],\end{aligned} \tag{15}$$

where

$$g=\Gamma(1/4)/\Gamma(3/4)\,.$$

Next we consider the term I_2. On making the substitution (11), it becomes

$$I_2 = -\frac{mD}{12\pi\eta}\,\frac{\mathrm{d}}{\mathrm{d}E}\int\limits_{-\omega_0}^{\omega_0} \frac{[(4+1/m)\,\omega^3 + 3\,\omega^2](1+\omega)^{1/m}}{(\omega_0{}^4-\omega^4)^{1/2}}\,\mathrm{d}\omega\,.$$

Proceeding in a similar manner as in the case of I_1, we obtain

$$I_2 = -\frac{\omega_0{}^{-3}}{6\sqrt{\pi}\,\eta}\,\frac{1+1/m}{\Gamma(1-1/m)}\sum_{k=0}^{\infty}\frac{\Gamma(-1-1/m+2k)\,\Gamma(k/2+7/4)}{\Gamma(1+2k)\,\Gamma(k/2+1/4)}\,\omega_0{}^{2k}, \quad |\omega_0| < 1\,. \tag{16}$$

This we can rewrite as

$$I_2 = -\frac{1}{6\sqrt{\pi}\,\eta}\,\frac{1+1/m}{\Gamma(1-1/m)}\left[\omega_0{}^{-3}\sum_{k=0}^{\infty}\frac{\Gamma(-1-1/m+4k)\,\Gamma(k+7/4)}{\Gamma(1+4k)\,\Gamma(k+1/4)}\,(\omega_0{}^4)^k\right.$$

$$\left. + \,\omega_0{}^{-1}\sum_{k=0}^{\infty}\frac{\Gamma(1-1/m+4k)\,\Gamma(k+9/4)}{\Gamma(3+4k)\,\Gamma(k+3/4)}\,(\omega_0{}^4)^k\right]$$

or as

$$I_2 = -\frac{1}{\eta\sqrt{\pi}}\left[\frac{m}{8g}\,\omega_0{}^{-3}\,{}_5F_4\left\{-\frac{1}{4}-\frac{1}{4m}, -\frac{1}{4m}, \frac{1}{4}-\frac{1}{4m}, \frac{1}{2}-\frac{1}{4m}, \frac{7}{4}; \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}; \omega_0{}^4\right\}\right. \tag{17}$$

$$\left. + \frac{5\,(1+1/m)\,g}{192}\,\omega_0{}^{-1}\,{}_5F_4\left\{\frac{1}{4}-\frac{1}{4m}, \frac{1}{2}-\frac{1}{4m}, \frac{3}{4}-\frac{1}{4m}, 1-\frac{1}{4m}, \frac{9}{4}; \frac{3}{4}, \frac{3}{4}, \frac{5}{4}, \frac{3}{2}; \omega_0{}^4\right\}\right].$$

Finally, we evaluate I_3. The substitution (9) gives

$$I_3 = \frac{m^3D^3}{1440\pi\eta^3}\,\frac{\mathrm{d}^3}{\mathrm{d}E^3}\int\limits_{-\omega_0}^{\omega_0}\left[\left(4+\frac{1}{m}\right)\left(8-\frac{3}{m}\right)\omega^6 + 3\left(21-\frac{1}{m}\right)\omega^5 + 33\,\omega^4\right]\frac{(1+\omega)^{1+3/m}}{(\omega_0{}^4-\omega^4)^{1/2}}\,\mathrm{d}\omega$$

which leads to

$$I_3 = \frac{m^3}{2880\sqrt{\pi}\,\eta^3}\left[33\,\omega_0{}^{-9}\sum_{k=0}^{\infty}\frac{(-1-3/m)_{2k}\,\Gamma(k/2+5/4)}{(2k)!\,\Gamma(k/2-5/4)}\,\omega_0{}^{2k}\right.$$

$$+\,\omega_0{}^{-7}\sum_{k=0}^{\infty}\left\{\left(95+\frac{182}{m}-\frac{12}{m^2}\right)-\left(31+\frac{1}{m}+\frac{3}{m^2}\right)(2k)\right\} \tag{18}$$

$$\left.\cdot\,\frac{(-1-3/m)_{2k}\,\Gamma(k/2+7/4)}{(2k+1)!\,\Gamma(k/2-3/4)}\,\omega_0{}^{2k}\right], \quad |\omega_0| < 1\,.$$

In terms of hypergeometric functions this is expressible as

$$I_3 = \frac{m^3}{1440\sqrt{\pi}\,\eta^3}\left[\frac{165g}{128}\,\omega_0{}^{-9}\,{}_5F_4\left\{-\frac{1}{4}-\frac{3}{4m}, -\frac{3}{4m}, \frac{1}{4}-\frac{3}{4m}, \frac{1}{2}-\frac{3}{4m}, \frac{5}{4}; -\frac{5}{4}, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}; \omega_0{}^4\right\}\right.$$

$$-\frac{891\,(1+3/m)}{64g\;m}\,\omega_0{}^{-7}\,{}_5F_4\left\{\frac{1}{4}-\frac{3}{4m}, \frac{1}{2}-\frac{3}{4m}, \frac{3}{4}-\frac{3}{4m}, 1-\frac{3}{4m}, \frac{7}{4}; -\frac{3}{4}, \frac{3}{4}, \frac{5}{4}, \frac{3}{2}; \omega_0{}^4\right\}$$

$$-\left(95+\frac{182}{m}-\frac{12}{m^2}\right)\left(\frac{9}{32g}\,\omega_0{}^{-7}\right.$$

$${}_5F_4\left\{-\frac{1}{4}-\frac{3}{4m}, -\frac{3}{4m}, \frac{1}{4}-\frac{3}{4m}, \frac{1}{2}-\frac{3}{4m}, \frac{7}{4}; -\frac{3}{4}, \frac{1}{2}, \frac{3}{4}, \frac{5}{4}; \omega_0{}^4\right\}$$

$$\left.\left. + \frac{5\,(1+3/m)\,g}{256\,m}\,\omega_0{}^{-5}\,{}_5F_4\left\{\frac{1}{4}-\frac{3}{4m}, \frac{1}{2}-\frac{3}{4m}, \frac{3}{4}-\frac{3}{4m}, 1-\frac{3}{4m}, \frac{9}{4}; -\frac{1}{4}, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \omega_0{}^4\right\}\right)\right.$$

$$+\left(31+\frac{1}{m}+\frac{3}{m^2}\right)\left(\frac{5(1+3/m)\,g}{128\,m}\,\omega_0^{-5}\right.$$
$${}_5F_4\left\{\frac{1}{4}-\frac{3}{4m},\frac{1}{2}-\frac{3}{4m},\frac{3}{4}-\frac{3}{4m},1-\frac{3}{4m},\frac{9}{4};-\frac{1}{4},\frac{1}{2},\frac{5}{4},\frac{7}{4};\omega_0^4\right\}$$
$$-\frac{21\,(2-3/m)\,(1-9/m^2)}{320\,g\,m}\,\omega_0^{-3}$$
$$\left.{}_5F_4\left\{\frac{3}{4}-\frac{3}{4m},1-\frac{3}{4m},\frac{5}{4}-\frac{3}{4m},\frac{3}{2}-\frac{3}{4m},\frac{11}{4};\frac{1}{4},\frac{3}{2},\frac{7}{4},\frac{9}{4};\omega_0^4\right\}\right)\Bigg)\Bigg]\,. \tag{19}$$

4. The Case $m = 1$

The case $m = 1$ is of special interest because the second- and third-order terms admit of considerable simplification in this case. We only quote the final values of I_1, I_2 and I_3 obtained after simplification.

$$I_1=\frac{\eta}{\sqrt{\pi}}\left[\frac{2g}{3}\,\omega_0^3\;{}_2F_1\left\{1,\frac{5}{4};\frac{7}{4};\omega_0^4\right\}+\frac{24}{5g}\,\omega_0^5\;{}_2F_1\left\{1,\frac{7}{4};\frac{9}{4};\omega_0^4\right\}\right];$$

$$I_2=-\frac{1}{96\sqrt{\pi}\,\eta}\left[\frac{12}{g}\,\omega_0^{-3}+5g\,\omega_0^{-1}\right];$$

$$I_3=\frac{1}{1024\sqrt{\pi}\,\eta^3}\left[\frac{11}{12}\,g\,\omega_0^{-9}-\frac{463}{5g}\,\omega_0^{-7}-\frac{47}{4}\,g\,\omega_0^{-5}+\frac{35}{3g}\,\omega_0^{-3}\right].$$

5. Results

The spacing of the energy levels depends on the form of the potential, and it is of obvious interest to study the pattern of the eigenvalues exhibited by the potential (5). We have considered two values for m, namely, 2 and 4, and three values for η, namely, 50, 25 and 15. The energy eigenvalues were calculated by solving (9). We shall find it convenient to depict the pattern of the spacing of the energy levels in reduced units. We define a ratio R_n by

$$R_n=\frac{E_n-E_{n-1}}{E_1-E_0}\,. \tag{20}$$

Figures 2 and 3 show R_n as a function of the quantum number n for $m = 2$ and 4, respectively. To provide a frame of reference for the results shown in these two figures, we note that the quartic potential (2) is intermediate between the square law potential of the simple harmonic oscillator and the square well potential of the particle in a one-dimensional box with infinitely high walls; in the former case, E_n is proportional to $(n+\frac{1}{2})$, and in the latter, to n^2. Thus $R_n = 1$ for the square law potential, and $R_n = 2n - 1$ for the square well potential.

It will be noticed in Figs. 2 and 3 that in all cases, R_n at first increases with n, reaches a maximum, and then decreases. For the simple quartic oscillator (2), R_n monotonically increases with n. For a fixed value of m, the position of the maximum is seen to vary regularly with η. The dependence of R_n on m can be examined by comparing the corresponding curves in Figs. 2 and 3; it is seen that the greater the value of m, the earlier (in terms of the quantum number) is the position of the maximum, and more rapid the decline.

It will be noticed from the expressions for I_1, I_2, and I_3 that each succeeding term in the WKBJ approximation differs in order from the previous one by a factor $1/\eta^2$. Thus we can anticipate that the accuracy of the eigenvalues, as obtained from these expressions, will diminish when very small values of η are involved.

It is well known that the WKBJ approximation improves as n increases. However, there is no exact method available to determine the accuracy of the eigenvalues obtained from the WKBJ method. Krieger et al. [20] have carried out a third-order WKBJ calculation for the quartic potential and have compared their eigenvalues with the accurate

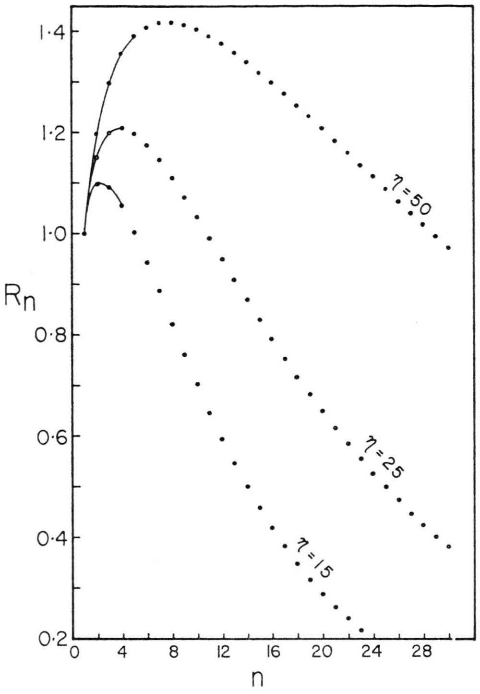

Fig. 2. The ratio R_n (Eq. (20)) as a funktion of the quantum number n. The constant m is put equal to 2. A few of the points have been joined merely as an aid to the eye.

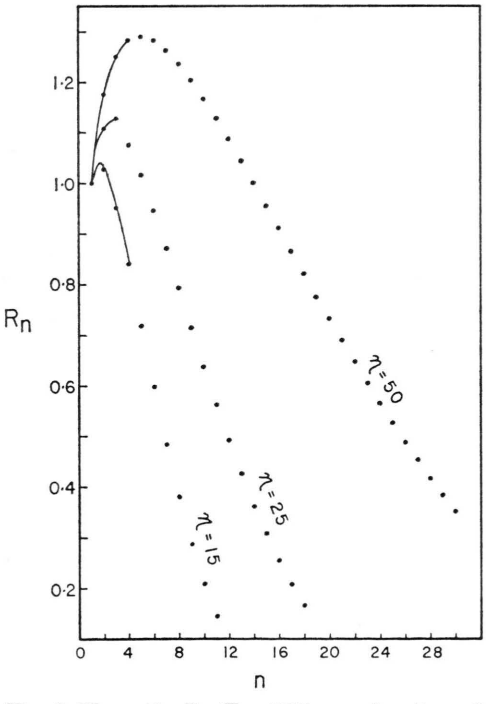

Fig. 3. The ratio R_n (Eq. (20)) as a function of the quantum number n. The constant m is put equal to 4. A few of the points have been joined merely as an aid to the eye.

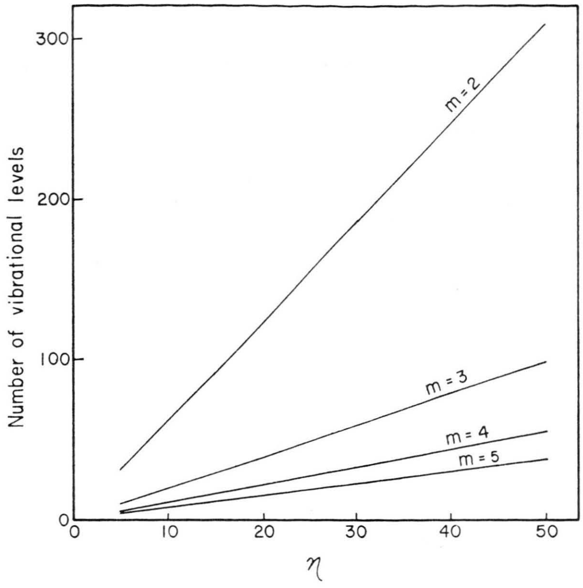

Fig. 4. Number of vibrational levels as a function of η, for $m = 2, 3, 4$, and 5.

eigenvalues obtained by Secrest et al. [9] from a numerical integration of the Schrödinger equation. This comparison shows that except for $n = 0$, the WKBJ values are in satisfactory agreement with the "exact" values, and the accuracy of the WKBJ values improves rapidly with n. It would appear to be reasonable to conjecture that a similar situation exists in our case.

For a given combination of m and η, only a certain number of bound vibrational states are possible. We have studied the maximum number of vibrational states as a function of m and η. Figure 4 shows the number of vibrational states as a function of η; curves are shown for $m = 2, 3, 4$, and 5. It is seen that for a fixed value of m, the number of vibrational states is almost a linear function of η in the range $5 \leqq \eta \leqq 50$.

We may add a remark concerning a suitable term to describe the type of potential that we have introduced. In analogy with the term *anharmonic*, we feel that the potential (5) may appropriately be described as an *anquartic* potential.

6. Possible Applications

Finally, we consider some possible applications of the proposed potential.

1. For some of the ring compounds, the ring-puckering vibrational energy levels can be described very well by a simple quartic potential [7] for low

values of the quantum number. It is possible that at high quantum numbers, departures from the simple quartic potential might occur. In such a situation it is likely that the potential (5) would be found to be useful.

2. For $m=1$, at large values of r, the potential (5) behaves as $-1/r$. This suggests the possibility of its being of use to represent the effective potential experienced by a valence electron in an atom.

3. It is generally accepted that the nuclear forces must have a property, similar to that of the chemical valence forces, that brings about "saturation". This type of force can be achieved in the simplest way by assuming a force which is strongly repulsive at short distances and attractive at a suitable range of distances. In most of the attempts to describe the nucleon-nucleon interaction [23—26], a repulsive core having a radius of about 0.45×10^{-13} cm has been assumed. The potential (5) satisfies the necessary requisites for the nucleon-nucleon interaction, in that it is similar to the interatomic potential, and in addition has a "hard" core. It has a certain amount of aesthetic beauty in that the "hard" core is obtained without introducing a discontinuous cut-off, as is the case with several of the prevalent internucleon potentials [23—26].

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