

Bohr Sommerfeld quantisation and molecular potentials

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Abstract We combine, within the Bohr Sommerfeld quantization rule, a systematic perturbation with asymptotic analysis of the action integral for potentials which support a finite number of bound states with $E < 0$ to obtain an interpolation formula for the energy eigenvalues. We find interpolation formulae for the Morse potential as well as potentials of the form $V = V_0 \left[\left(\frac{a}{x}\right)^{2k} - \left(\frac{a}{x}\right)^k \right]$. For $k = 6$ i.e. the well known Lennard Jones potential this yields results within 1 per cent of the highly accurate numerical values. For the Morse potential this procedure yields the exact answer. We find that the result for the Morse potential which approaches zero exponentially is the $k \rightarrow \infty$ limit of the Lennard Jones class of potentials.

Keywords Action integral · Perturbation theory · Asymptotic analysis · Interpolation formula · Morse potential · Lennard Jones potential

1 Introduction

It is quite common in quantum mechanics texts [1] to obtain the quantised energy levels of certain canonical systems from the action angle quantization which is also the Bohr Sommerfeld quantization condition [2]. This quantization scheme is successful

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in one dimension when the classical system shows a unique periodic orbit for a given energy (an example of an exception is the double well potential which has two possible periodic orbits for energies below the unstable maximum of the potential and the splitting of energy levels does not follow from the usual Bohr Sommerfeld Condition [3]). Quantization of the action integral along the periodic orbit leads to the condition (p is the momentum):

$$J(E) = \oint p(x)dx = nh \quad (1.1)$$

where $n = 1, 2, \dots$. Using the WKB method it can be argued [4] that n should really be $n + \alpha$ where α is a constant which for smooth potentials in one dimension turns out to be $1/2$. Then $n = 0$ can be included in the range of values of n . The potentials usually studied using this technique are the infinite square well, simple harmonic oscillator and the general class of oscillators with the potential $V(x) = \alpha|x|^k$, where k is an integer. It was shown by Robinett [5] that perturbation theory can be carried out on Eq. (1.1) and can yield almost trivially the correspondence principle limit of first order perturbation theory. In spite of its simplicity the Bohr Sommerfeld technique remains a popular area of investigation [6, 7]. Recent works deal with a two dimensional electron gas in a magnetic field [8] and issues related to 3-branes [9].

Our primary observation is that any potential $V(x)$ with two turning points which also possesses a minimum can be expanded about the same. If the minimum is at $x = x_0$ and $V(x_0) = V_0$ then the expansion will acquire the form

$$\begin{aligned} V(x) &= V_0 + \frac{1}{2}V''(x_0)(x - x_0)^2 + \frac{1}{3!}V'''(x_0)(x - x_0)^3 + \frac{1}{4!}V''''(x_0)(x - x_0)^4 + \dots \\ &= V_0 + \frac{1}{2}m\omega^2(x - x_0)^2 + \frac{\alpha}{3}(x - x_0)^3 + \frac{\beta}{4}(x - x_0)^4 + \dots \end{aligned} \quad (1.2)$$

where ω , α and β are easily identified.

With $V(x)$ expanded as above it will be our aim to evaluate the action $J(E) = \oint p dx$ which equals $\oint \sqrt{2m(E - V(x))} dx$, perturbatively about the quadratic term and express it as a power series in α , β etc. Using Eq. 1.1 we can now obtain E as a power series in α , β . . . We will see that for quite a few potentials the coefficients α , β etc conspire to cause the perturbation theory to terminate and we get an exact answer.

Using the above perturbation theory, we will use the Bohr–Sommerfeld scheme for molecular potentials (Morse potential [10, 11], Lennard Jones potential [12–16] etc) where a finite number of bound states exist to take care of the possibility of dissociation. Given a potential which supports a finite number of bound states e.g. the Lennard Jones class of potentials $V = V_0[(\frac{a}{x})^{2k} - (\frac{a}{x})^k]$ where V_0 and a are constants we evaluate the action integral by perturbation theory in the anharmonic terms of Eq. (1.2). With $E < 0$ we next evaluate the action integral asymptotically for $E \approx 0$. This fixes the largest allowed value n_0 of the quantum number. It also yields the dependence of the energy eigenvalue on the quantum number for $E \approx 0$. We interpolate between the energy expression obtained from perturbation theory and the expression that holds near n_0 to arrive at a final expression for the energy eigenvalue. For the Morse potential this actually yields the exact answer.

In Sect. 2 we set up the basic perturbation theory. In Sect. 3 we treat the Morse potential and in Sect. 4 we deal with the Lennard Jones class of potentials. A brief summary is given in Sect. 5.

2 The perturbation theory

In this section we evaluate the action integral J for the basic anharmonic oscillator having the potential $V(x) = \frac{1}{2}m\omega^2x^2 + \frac{\alpha}{3}x^3 + \frac{\beta}{4}x^4$ using perturbation theory. This requires a perturbative evaluation of the integral

$$J = 2\sqrt{2m} \int_{a_l}^{a_r} \sqrt{E - \frac{1}{2}m\omega^2x^2 - \frac{\alpha x^3}{3} - \frac{\beta x^4}{4}}. \tag{2.1}$$

where a_l and a_r are the left and right turning points respectively. Since the oscillations are about the origin $a_l < 0$ and $a_r > 0$. If the amplitude of motion is a (i.e. the kinetic energy vanishes at $a = 0$), then

$$E = \frac{1}{2}m\omega^2a^2 + \frac{\alpha a^3}{3} + \frac{\beta a^4}{4} \tag{2.2}$$

The left and right turning points are the negative and positive values of ‘ a ’ that satisfy Eq. (2.2). Our first task is a_l and a_r . To this end we expand

$$a_{l,r} = a_0 + \alpha a_1 + \alpha^2 a_2 + \beta a'_1. \tag{2.3}$$

Inserting in Eq. (2.2)

$$\begin{aligned} E &= \frac{1}{2}m\omega^2 \left[a_0^2 + 2\alpha a_1 a_0 + 2a_0 a_2 \alpha^2 + a_1^2 \alpha^2 + 2a_0 a'_1 \beta + \dots \right] \\ &\quad + \frac{\alpha}{3} \left[a_0^3 + 3\alpha a_0^2 a_1 \right] + \frac{\beta}{4} a_0^4 + \dots \\ &= \frac{1}{2}m\omega^2 a_0^2 + \alpha \left[m\omega^2 a_0 a_1 + \frac{a_0^3}{3} \right] + \alpha^2 \left[m\omega^2 a_0 a_2 + \frac{1}{2}m\omega^2 a_1^2 + a_0^2 a_1 \right] \\ &\quad + \beta \left[m\omega^2 a_0 a'_1 + \frac{a_0^4}{4} \right] + \dots \end{aligned} \tag{2.4}$$

Equating identical powers of α and β from either side of Eq. (2.4)

$$a_0^2 = \frac{2E}{m\omega^2} \quad (2.5)$$

$$a_1 = -\frac{a_0^2}{3m\omega^2} \quad (2.6)$$

$$a_0 a_2 = \frac{5}{18} \left(\frac{a_0^2}{m\omega^2} \right)^2 \quad (2.7)$$

$$a_1' = -\frac{a_0^3}{4m\omega^2} \quad (2.8)$$

There are two roots of a_0 from Eq. (2.5), the positive corresponds to a_r and the negative to a_l . Accordingly, we can write down the perturbation expression for the two turning points as

$$a_r = |a_0| - \frac{\alpha a_0^2}{3m\omega^2} + \frac{5}{18} \alpha^2 \left(\frac{a_0^2}{m\omega^2} \right)^2 \frac{1}{|a_0|} - \beta \frac{|a_0|^3}{4m\omega^2} \quad (2.9)$$

$$a_l = -|a_0| - \frac{\alpha a_0^2}{3m\omega^2} - \frac{5}{18} \alpha^2 \left(\frac{a_0^2}{m\omega^2} \right)^2 \frac{1}{|a_0|} + \beta \frac{|a_0|^3}{4m\omega^2}. \quad (2.10)$$

Having found the turning points, we can now evaluate J in perturbation theory. Accordingly, Eq (2.1) is written as

$$\begin{aligned} J &= 2\sqrt{2m} \int_{a_l}^{a_r} \sqrt{\frac{1}{2}m\omega^2 (a^2 - x^2) + \frac{\alpha}{3} (a^3 - x^3) + \frac{\beta}{4} (a^4 - x^4)} \\ &= 2m\omega \int_{a_l}^{a_r} \sqrt{a^2 - x^2} \left[1 + \frac{\alpha}{3m\omega^2} \frac{a^3 - x^3}{a^2 - x^2} - \frac{1}{18} \left(\frac{\alpha}{m\omega^2} \right)^2 \left(\frac{a^3 - x^3}{a^2 - x^2} \right)^2 \right. \\ &\quad \left. + \frac{\beta}{4m\omega^2} (a^2 + x^2) + \dots \right] dx \end{aligned} \quad (2.11)$$

Now,

$$\begin{aligned} \int_{a_l}^{a_r} \sqrt{a^2 - x^2} dx &= \int_{a_l}^0 \sqrt{a_l^2 - x^2} dx + \int_0^{a_r} \sqrt{a_r^2 - x^2} dx \\ &= \frac{\pi}{4} (a_l^2 + a_r^2) \\ &= \frac{\pi}{4} \left[2a_0^2 + \frac{4}{3} \alpha^2 \left(\frac{a_0^2}{m\omega^2} \right)^2 - \beta a_0^4 + \dots \right] \end{aligned} \quad (2.12)$$

Similarly,

$$\begin{aligned} \int_{a_l}^{a_r} \frac{a^3 - x^3}{\sqrt{a^2 - x^2}} &= \frac{\alpha}{3m\omega^2} \left(\frac{\pi}{2} - \frac{2}{3}\right) (a_r^3 - |a_l|^3) \\ &= -\frac{2}{3}\alpha^2 \left(\frac{a_0^2}{m\omega^2}\right)^2 \left(\frac{\pi}{2} - \frac{2}{3}\right) + \dots \end{aligned} \tag{2.13}$$

Working to $O(\alpha^2)$ and $O(\beta)$ implies that the remaining integrals in Eq. (2.11) can be evaluated from $-|a_0|$ to $|a_0|$ and thus

$$-\frac{1}{18} \left(\frac{\alpha}{m\omega^2}\right)^2 \int_{-|a_0|}^{|a_0|} \frac{(a_0^3 - x^3)^2}{(a_0^2 - x^2)^{3/2}} = -\frac{a_0^4}{9} \left(\frac{\alpha}{m\omega^2}\right)^2 \left(4 - \frac{15\pi}{16}\right) \tag{2.14}$$

and

$$\frac{\beta}{4m\omega^2} \int_{-|a_0|}^{|a_0|} \sqrt{a_0^2 - x^2} (a_0^2 + x^2) dx = \frac{\beta}{4m\omega^2} \frac{5\pi a_0^4}{8}. \tag{2.15}$$

Using Eq. (2.5) and putting together the results from Eq. (2.12) to Eq. (2.15) we have

$$J = \frac{2\pi E}{\omega} + \frac{5\pi\alpha^2}{6m^3\omega^7} E^2 - \frac{3\pi\beta}{4\omega} \frac{E^2}{m^2\omega^4} + \dots \tag{2.16}$$

We now use the quantization condition $J = nh$ and solve for E perturbatively by expanding

$$E = E_0 + \alpha E_1 + \alpha^2 E_2 + \beta E_2' + \dots \tag{2.17}$$

Using the same steps as for the turning points, we get

$$E = n\hbar\omega - \frac{5}{12} \frac{\alpha^2}{m^3\omega^4} n^2 \hbar^2 + \frac{3}{8} \frac{\beta}{m^2\omega^2} n^2 \hbar^2 \tag{2.18}$$

This is one of the central results which we will use later.

3 The Morse potential

The Morse potential, which describes the interaction between the neutral atoms of a diatomic molecule is written as

$$V(x) = V_0(e^{-2ax} - 2e^{-ax}) = -V_0 + V_0(1 - e^{-ax})^2. \tag{3.1}$$

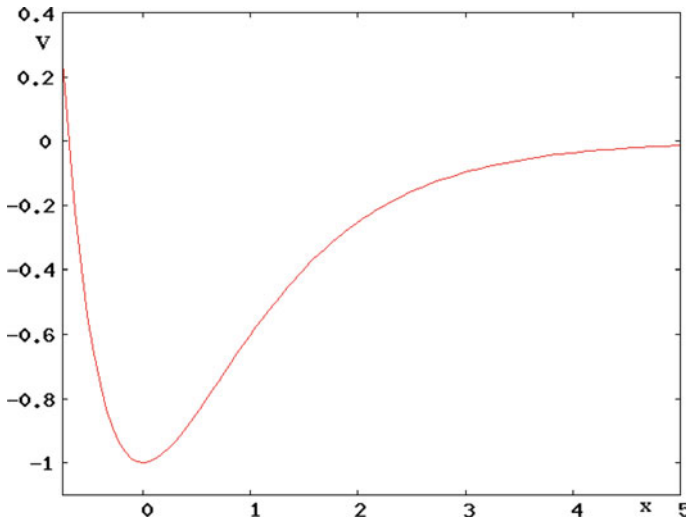


Fig. 1 Morse potential

The potential is shown in Fig. 1. Bound states are expected for $E < 0$. The minimum of the potential is at $x = 0$ and we can expand the RHS of Eq. (3.1) about $x = 0$ to write

$$V(x) = -V_0 + V_0(ax)^2 \left(1 - ax + \frac{7}{12}a^2x^2 + \dots \right) \quad (3.2)$$

In Sect. 2 we considered the basic anharmonic oscillator.

$$V(x) = \frac{1}{2}m\omega^2x^2 + \frac{\alpha}{3}x^3 + \frac{\beta}{4}x^4 + \dots \quad (3.3)$$

Comparing Eq. (3.2) and (3.3) we note that apart from a shift of $-V_0$ we can identify

$$\omega^2 = \frac{2V_0a^2}{m}, \quad \alpha = -3V_0a^3, \quad \beta = \frac{7V_0a^4}{3} \quad (3.4)$$

Using Eq. (2.18) we can write down the energy of the anharmonic oscillator to $O(\alpha^2)$ and $O(\beta)$ using the identifications in Eq. (3.4) as

$$E' = \left(n + \frac{1}{2} \right) \hbar a \sqrt{\frac{2V_0}{m}} - \frac{1}{2} a^2 \frac{(n + 1/2)^2}{m} \hbar^2 \quad (3.5)$$

To get the full energy we need to add the shift $-V_0$ and this gives the total energy as

$$E = - \left[\sqrt{V_0} - \left(n + \frac{1}{2} \right) \frac{\hbar a}{\sqrt{2m}} \right]^2 \quad (3.6)$$

correct to this order in perturbation theory.

We now turn to the asymptotic analysis i.e. the situation for $E \approx 0$.
 With the substitution $e^{-ax} = y$ the action integral becomes

$$J(E) = 2 \int_{y_1}^{y_2} \frac{1}{y} \sqrt{\frac{2mV_0}{a^2} \left(\frac{E}{V_0} + 2y - y^2 \right)} dy \tag{3.7}$$

where y_1 and y_2 are the zeroes of the integrand easily found to be

$$y_{1,2} = 1 \mp \sqrt{1 + \frac{E}{V_0}} \tag{3.8}$$

Setting $E = 0$ yields n_0 from $J(0) = (n_0 + \frac{1}{2}) h$ and from Eq. (3.7) we immediately see

$$n_0 + \frac{1}{2} = \sqrt{\frac{2mV_0}{a^2 \hbar^2}} \tag{3.9}$$

We note that this is the same result that one gets from the perturbation theory of Eq. (3.6). We now need to explore the integral in Eq. (3.7) for $E/V_0 \approx 0$. Since E is negative we write $E/V_0 = -\epsilon$ ($\epsilon > 0$) and note that for $\epsilon \ll 1$

$$y_1 \approx \frac{\epsilon}{2} \quad \text{and} \quad y_2 = 2 \tag{3.10}$$

The primary contribution to the integral in Eq. (3.7) has to come from the region $y \ll 1$, i.e. from the end $y \approx y_1$ and we need to focus on this end. We write Eq. (3.7) and expand around $\epsilon = 0$ as

$$\begin{aligned} J(E) &= 2\sqrt{\frac{2mV_0}{a^2}} \int_{\epsilon/2}^2 \frac{1}{y} \sqrt{2y - y^2 - \epsilon} dy \\ &= 2\sqrt{\frac{2mV_0}{a^2}} \left(\int_{\epsilon/2}^2 \frac{1}{y} \sqrt{2y - y^2} dy - \frac{\epsilon}{2} \int_{\epsilon/2}^2 \frac{1}{y\sqrt{2y - y^2}} dy + \dots \right) \\ &= 2\sqrt{\frac{2mV_0}{a^2}} \left(\int_0^2 \frac{\sqrt{2y - y^2}}{y} dy - \int_0^{\epsilon/2} \frac{\sqrt{2y - y^2}}{y} dy - \frac{\epsilon}{2} \int_{\epsilon/2}^2 \frac{1}{y\sqrt{2y - y^2}} dy \right) \\ &= \left(n_0 + \frac{1}{2} \right) h - 2\sqrt{\frac{2mV_0}{a^2}} \left(\int_0^{\epsilon/2} \frac{\sqrt{2y - y^2}}{y} dy + \epsilon \int_{\epsilon/2}^2 \frac{1}{y\sqrt{2y - y^2}} dy \right) \end{aligned} \tag{3.11}$$

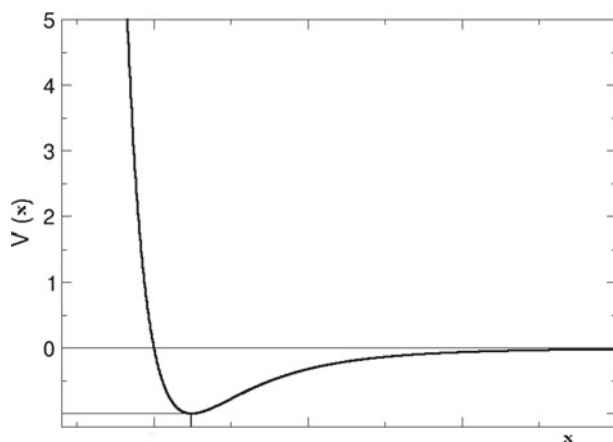


Fig. 2 Lennard Jones potential

In evaluating the integrals in the parentheses in Eq. (3.10) our interest is in the range $y \ll 1$ and hence $y \gg y^2$. Dropping the y^2 in the integrand shows that the leading behaviour of both integrals is $\epsilon^{1/2}$ and thus, to the lowest order in ϵ , has the structure

$$J(E) = \left(n_0 + \frac{1}{2}\right) h - C\epsilon^{1/2} + \dots \quad (3.12)$$

where C is a numerical constant which we have not determined. Since $J(E) = (n + \frac{1}{2})h$, Eq. (3.11) shows that for $n \approx n_0$,

$$E = -V_0 C^2 (n_0 - n)^2. \quad (3.13)$$

This is the asymptotic form. Fortuitously the perturbation theory answer of Eq. (3.6) has exactly this structure and thus the interpolation in this case is Eq. (3.6) itself. No wonder that Eq. (3.6) is the exact answer for the Morse potential. In the next section we will find that to match the perturbation theory and the asymptotic result for the Lennard Jones potential, an interpolation formula will have to be constructed.

4 The Lennard Jones variety of potentials

In this section, we focus on the class of potentials

$$V(x) = V_0 \left[\left(\frac{a}{x}\right)^{2k} - \left(\frac{a}{x}\right)^k \right] \quad (4.1)$$

For $k = 6$, this gives the well known Lennard Jones potential, shown in Fig. 2.

Table 1 Comparison of energy eigenvalues obtained from Eq. (4.5) with exact numerical values

n	$4E/V_0$ from Eq. (4.9) $x - (10^{-3})$	$4E/V_0$ exact. $x - (10^{-3})$
0	941	941
1	830	830
2	728	728
3	636	634
4	551	548
5	477	470
10	239	186

Expanded about the minimum at x_0 given by

$$2 \left(\frac{a}{x_0} \right)^k = 1 \tag{4.2}$$

the potential takes the form

$$V(x) = -\frac{V_0}{4} + \frac{k^2}{4} V_0 \left(\frac{x - x_0}{x_0} \right)^2 - \frac{V_0}{4} k^2 (k + 1) \left(\frac{x - x_0}{x_0} \right)^3 + V_0 \frac{k^2 (k + 1) (7k + 11)}{48} \left(\frac{x - x_0}{x_0} \right)^4 + \dots \tag{4.3}$$

which is an anharmonic oscillator of the type discussed in Sect. 2. Comparing the structure of Eq. 4.3 with the anharmonic potential

$$V(x) = \frac{1}{2} m \omega^2 x^2 + \frac{\alpha}{3} x^3 + \frac{\beta}{4} x^4$$

we have

$$\omega = \frac{k}{\sqrt{22}^{1/k}} \sqrt{\frac{V_0}{ma^2}}, \alpha = -\frac{3V_0}{4} \frac{k^2(k+1)}{a^2 2^{3/k}}, \beta = \frac{V_0}{12} \frac{k^2(k+1)(7k+11)}{a^4 2^{4/k}} \tag{4.4}$$

Using Eq. (2.18) and adding in the part $-\frac{V_0}{4}$ to obtain the total energy, we have

$$\frac{4E}{V_0} = -1 + 4 \left(n + \frac{1}{2} \right) \frac{\hbar\omega}{V_0} - \frac{2(2k+1)(k+1)}{k^2} \left[\left(n + \frac{1}{2} \right) \frac{\hbar\omega}{V_0} \right]^2 + \dots \tag{4.5}$$

We can compare this result with the numerical values [17] given in literature for $k = 6$, the Lennard Jones case. All the numerical results are for $\frac{\hbar\omega}{V_0} = 0.03$ and a comparison between accurate numerical results and our perturbation formula is shown in Table 1.

We notice that the accuracy starts deteriorating at $n = 5$, and the error is already greater than 25% at $n = 10$. This indicated that an asymptotic analysis has to be carried out.

We want to examine the asymptotic behavior of

$$J = 2 \int_{x_1}^{x_2} \sqrt{2m \left\{ E - V_0 \left[\left(\frac{a}{x} \right)^{2x} - \left(\frac{a}{x} \right)^k \right] \right\}} dx \quad (4.6)$$

as we did for the Morse potential in Sect. 2 as $E \rightarrow 0$. In Eq. (4.6), x_1 and x_2 and the turning points of motion with $x_1 < x_2$. Since $E4$ is negative, we let $E/V_0 = -\epsilon$ ($\epsilon > 0$) and substituting $y = \left(\frac{a}{x} \right)^k$, we rewrite Eq. (4.6) as.

$$J = \frac{2\sqrt{2mV_0\alpha^2}}{k} \int_{y_1}^{y_2} \sqrt{y - y^2 - |\epsilon|} \frac{dy}{y^{1+\frac{1}{k}}} \quad (4.7)$$

With the two turning points $y_{1,2}$ ($y_1 < y_2$) given by

$$y_{1,2} = \frac{1}{2} \left\{ 1 \mp \sqrt{1 - 4\epsilon} \right\} \quad (4.8)$$

As $\epsilon \rightarrow 0$, $y_1 \rightarrow \epsilon$ and $y_2 \rightarrow 1$ and the integral of Eq. (4.7) diverges if $k < 2$ and is finite for $k > 2$. If the integral diverges, then the potential supports an infinite number of bound states while a finite number implies a finite number of bound states. Accordingly, we need to treat the two cases separately.

Case (A): $k < 2$

In this case, the integral in Eq. (4.7) diverges for $\epsilon \rightarrow 0$ and in extracting this divergent behavior from Eq. (4.7) we can drop the y^2 term in comparison to y . The integral is thus approximated as

$$J \cong 2 \frac{\sqrt{2mV_0\alpha^2}}{k} |\epsilon|^{\frac{1}{2}-\frac{1}{k}} \int_1^{1/\epsilon} \sqrt{z-1} \frac{dz}{z^{1+1/k}} \quad (4.9)$$

Since $\epsilon \rightarrow 0$ we can set the upper limit equal to infinity and thus get

$$J \cong \frac{\sqrt{2\pi V_0\alpha^2}}{k} \frac{\Gamma\left(\frac{1}{k} - \frac{1}{2}\right)}{\Gamma\left(\frac{1}{k} + 1\right)} \epsilon^{\frac{1}{2}-\frac{1}{k}} \quad (4.10)$$

For $k < 2$, this is the dominant contribution to J as $\epsilon \rightarrow 0$. Using the Bohr Sommerfeld quantization condition, we have for $\epsilon \rightarrow 0$,

$$\left| \frac{4E}{V_0} \right|^{\frac{1}{2}-\frac{1}{k}} = 2^{2-\frac{1}{k}} \sqrt{\pi} \frac{\Gamma\left(1 + \frac{1}{k}\right)}{\Gamma\left(\frac{1}{k} - \frac{1}{2}\right)} \left(n + \frac{1}{2} \right) \frac{\hbar\omega}{V_0} \quad (4.11)$$

Thus for $\frac{\hbar\omega}{V_0} \gg 1$, we have Eq. (4.11) and for $\frac{\hbar\omega}{V_0} \ll 1$, we have Eq. (4.5). The simplest formula connecting both ends is

$$\frac{4E}{V_0} = - \frac{1}{\left\{ 1 + 2^{2-\frac{1}{k}} \frac{\sqrt{\pi}\Gamma\left(1+\frac{1}{k}\right)}{\Gamma\left(\frac{1}{k}-\frac{1}{2}\right)} \left(n + \frac{1}{2}\right) \frac{\hbar\omega}{V_0} \right\}^{\frac{2k}{2-k}}} \tag{4.12}$$

For $k = 1$ in particular

$$\frac{4E}{V_0} = - \frac{1}{\left[1 + (2n + 1) \frac{\hbar\omega}{V_0} \right]^2} \tag{4.13}$$

which exactly reproduces Eq. (4.5) on expansion. In this case the integral for J can be exactly evaluated and Eq. (4.13) is the exact answer. For other values of k , a simple formula like the one of Eq. (4.12) would not be adequate since on expanding, even the first term in $\left(n + \frac{1}{2}\right) \frac{\hbar\omega}{V_0}$ is not correctly reproduced. We do not concern ourselves with this any more but rather turn our attention to $k > 2$, i.e. the situation where a finite number of bound states exist.

Case (B): $k > 2$

We return to Eq. (4.7) and examine it for $\epsilon \rightarrow 0$ for $k > 2$. we note that for $\epsilon = 0$, the integral has a finite value which will clearly be the leading term of J . This finite value, J_0 , is found as

$$\begin{aligned} J_0 &= 2 \frac{\sqrt{2mV_0}a^2}{k} \cdot \int_0^1 \sqrt{y(1-y)} \cdot \frac{dy}{y^{1+\frac{1}{k}}} \\ &= \frac{\sqrt{\pi}}{2^{1/k}} \cdot \frac{\Gamma\left(\frac{1}{2} - \frac{1}{k}\right)}{\Gamma\left(2 - \frac{1}{k}\right)} \frac{V_0}{\omega} \end{aligned} \tag{4.14}$$

This immediately yields the value n_0 of n for which $\epsilon = 0$ since $J_0 = \left(n_0 + \frac{1}{2}\right) h$.

To find the correction to J_0 for $\epsilon \ll 1$ we proceed exactly as in Sect. 3 (see Eq. (3.10)). The turning points for $\epsilon \ll 1$ are $y_1 \approx \epsilon$ and $y_2 \approx 1$ and we can expand the integral in Eq. (4.7) as

$$\begin{aligned} I &= \int_{\epsilon}^1 \frac{\sqrt{y - y^2 - \epsilon}}{y^{1+1/k}} dy \\ &= \int_0^1 \frac{\sqrt{y - y^2}}{y^{1+1/k}} dy - \int_0^{\epsilon} \frac{\sqrt{y - y^2}}{y^{1+1/k}} dy - \epsilon \int_{\epsilon}^1 \frac{1}{\sqrt{y - y^2} (y^{1+1/k})} dy \end{aligned} \tag{4.15}$$

Since the dominant part of I comes from the region $y \ll 1$ for $\epsilon \ll 1$ one can drop the y^2 in comparison with y in the last two terms and find

$$I = I_0 - I_1 \epsilon^{1/2-1/k} + \dots \quad (4.16)$$

We thus arrive at

$$J = J_0 - C \epsilon^{1/2-1/k} + \dots \quad (4.17)$$

where C is a constant which we have not tried to determine.

We now have the following facts :

- (i) for $(n + \frac{1}{2}) \frac{\hbar\omega}{V_0} \ll 1$, the perturbation expansion of Eq. (4.5)
- (ii) $E = 0$ at $n = n_0$ such that

$$n_0 + \frac{1}{2} = \frac{1}{2^{1+1/k} \sqrt{\pi}} \frac{\Gamma(\frac{1}{2} - \frac{1}{k})}{\Gamma(2 - \frac{1}{k})} \frac{V_0}{\hbar\omega} \quad (4.18)$$

- (iii) near n_0 , E vanishes as $(n_0 - n)^{2k/k-2}$.

We now propose the interpolation formula

$$\frac{4E}{V_0} = - \frac{\left(1 - \frac{n+1/2}{n_0+1/2}\right)^{2k/k-2}}{1 + \alpha(n+1/2) + \beta(n+1/2)^2} \quad (4.19)$$

where the parameters α and β are to be obtained from the condition that the perturbation expansion of Eq. (4.5) is reproduced when Eq. (4.19) is expanded in powers of $(n + 1/2)$. This leads to

$$\alpha + \frac{2k}{k-2} \frac{1}{n_0 + 1/2} = \frac{4\hbar\omega}{V_0} \quad (4.20a)$$

$$\alpha^2 - \beta + \frac{2\alpha k}{k-2} \frac{1}{n_0 + 1/2} + \frac{k(k+2)}{(k-2)^2} \left(\frac{1}{n_0 + 1/2}\right)^2 = \frac{(2k+1)(2k+2)}{k^2} \left(\frac{\hbar\omega}{V_0}\right)^2 \quad (4.20b)$$

To compare with numerical results we choose the most popular situation of $k = 6$ (Lennard Jones potential). Extensive numerical results exist for $\hbar\omega/V_0 = 0.03$ for which we get, $\alpha = -0.00605$ and $\beta = 2.7 \times 10^{-5}$ from Eqs. 4.20a, and 4.20b. The resulting values of $4E/V_0$ are shown in Table 2 where the exact numerical values are also exhibited.

The agreement is to within 0.1%, which is a significant fact for an analysis which is so straightforward.

We end this paper by noting a curious phenomenon. If $k \rightarrow \infty$ then Eq. (4.18) gives $n_0 + \frac{1}{2} = \frac{V_0}{2\hbar\omega}$ and now from Eqs. 4.20a, and 4.20b we find that $\alpha = \beta = 0$ in the limit $k \rightarrow \infty$. The energy of Eq. (4.19) is the same as the energy of the Morse potential, as

Table 2 Comparison of energy eigenvalues obtained from Eq. (4.19) with exact numerical values

n	E (Exact numerical) $X - (10^{-5})$	E (Fitting formula) $X - (10^{-5})$
0	94104	94113
1	83000	83007
1	72764	72770
3	63369	63373
4	54785	54788
5	46982	46984
6	39930	39932
7	33596	33598
8	27947	27950
9	22951	22954
10	18572	18576
11	14775	14779
12	11523	11526
13	08777	08779
14	06498	06500
15	04647	04647
16	03181	03180
17	02059	02055
18	01235	01231
19	00666	00661
20	00305	00300
21	00105	00102
22	00019	00019
23	00000 (to given accuracy)	00000 (to given accuracy)

in Eq. (3.6). Since the Morse potential approaches zero exponentially fast, it can be thought of as a $k \rightarrow \infty$ limit of a power law potential.

5 Conclusion

It is the simplicity of the Bohr Sommerfeld quantization scheme that has kept it popular [18, 19] even now. We have shown that this condition can be effectively used for a wide variety of potentials where it has not traditionally been applied. There are two essential ingredients in our calculation. The first is the expansion of the potential about its minimum. This expression gives an anharmonic oscillator and treating the anharmonic terms as perturbation we can find a perturbative form for the energy. The perturbation technique works well if the energy is close to a minimum. It needs to be supplemented by an analysis which holds near the maximum bound state energy. If the maximum possible value of the bound state energy is E_{\max} then the action can be evaluated at $E = E_{\max}$ and this allows us to get the highest possible quantum num-

ber n_{\max} . Calculation of the energy near n_{\max} can be combined with the perturbation expansion in a Pade type interpolation formula to yield an effective expression for the energy. This is what happened here. We have done it for the Morse potential and the Lennard Jones class of potentials. While we have not shown it here, the perturbation theory developed here gives exact answers for the Pöschel Teller and the Rosen Morse [20] potentials as well.

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