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Lindstedt Poincare technique applied to molecular potentials

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Abstract The Lindstedt–Poincare technique has traditionally been used to deal with oscillators with power-law potentials. We show how this method can be extended to deal with molecular potentials for which the frequency goes to zero as the energy approaches zero. The extension requires the use of an asymptotic analysis which is combined with perturbation theory. For the Morse potential, we get an exact answer while for the Lennard Jones class of potentials $\mathrm{V} = \mathrm{V}_0\left[\left(\frac{\mathrm{a}}{\mathrm{x}}\right)^{2\mathrm{n}} - \left(\frac{\mathrm{a}}{\mathrm{x}}\right)^{\mathrm{n}}\right]$, the answer is generally approximate with some values of n giving exact results. For the widely studied case, $\mathrm{n} = 6$, our approximation gives better than 1% accuracy at the lowest order of calculation. We show that as $\mathrm{n} \to \infty$, the result tends to that for the Morse potential. We also point out that the time period obtained by us can be used to obtain the quantum mechanical energy levels of these potentials within the Bohr-Sommerfeld scheme.

Keywords Molecular potentials · Lindstedt Poincare perturbation theory · Asymptotic analysis · Morse potential · Lennard Jones potential · Bohr Sommerfeld quantisation

1 Introduction

It is well known that for the Morse potential $\mathrm{V} = \mathrm{V}_0\left(\mathrm{e}^{-2\mathrm{ax}} - 2\mathrm{e}^{-\mathrm{ax}}\right)$ there is a periodic motion for negative total energy E. The potential is shown in Fig. 1 and as shown

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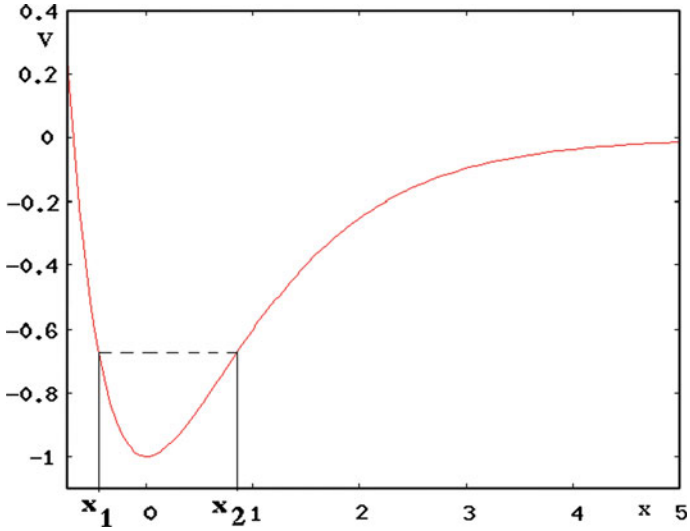

Fig. 1 The Morse potential

by the dashed line corresponding to a negative value of E, the motion is bounded between the turning points x_1 and x_2.

For $E > 0$ the motion is clearly unbounded. For $E = 0$, the dividing line between bounded and unbounded motions, the time period becomes infinitely big. The answer for the time period T for this case has been worked out in the mechanics text of Jose and Saletan [1] and is found to be $T = \frac{\pi}{a}\sqrt{-\frac{2}{E}}$. As expected the time period diverges as $E \to 0$. The singularity is of the power law variety. This is in contrast to another well known case of divergent period which occurs for the potential $V(x) = -x^2/2 + x^4/4$ shown in Fig. 2.

This is a double well potential and for $E < 0$, the oscillations occur in one well with turning points x_1 and x_2 and for $E > 0$ oscillations take place across the two wells. For the dividing case of $E = 0$ the frequency goes to zero. However the behaviour near $E = 0$ is given by T proportional to $\ln(1/|E|)$ as opposed to the power law for the Morse potential. For the potential $V(x) = V_0\left[\frac{x^2}{2} - \frac{x^3}{3} - \frac{1}{6}\right]$ shown in Fig. 3 the orbits are unbounded for $E > 0$ and bounded for $E < 0$. As $E \to 0$ the time period diverges as $\ln(1/|E|)$.

We first need to clarify the reason behind the two different behaviours—the power law divergence of the Morse potential and the potentials of Figs. 2 and 3. Writing the oscillations as a dynamical system we find that

$$\dot{x} = y$$
$$\dot{y} = -V'(x)$$

The fixed points (equilibrium points) are given by the zeroes of $V'(x)$ i.e. the extrema of $V(x)$. While the Morse potential has only one equilibrium point the other potentials

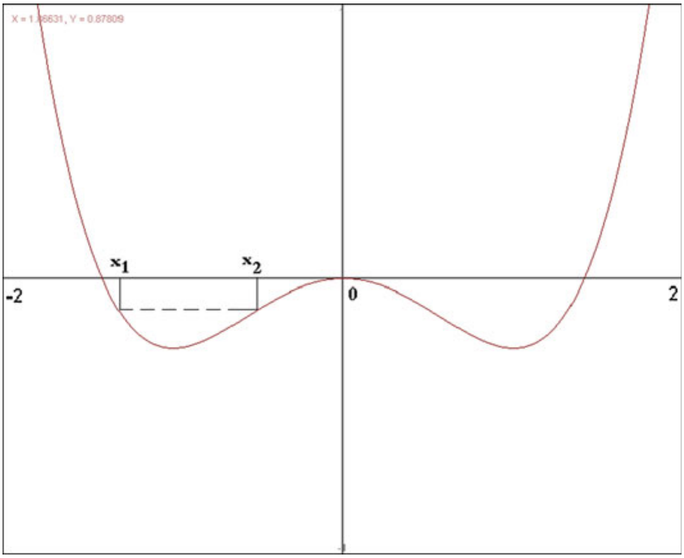

Fig. 2 Double well potential

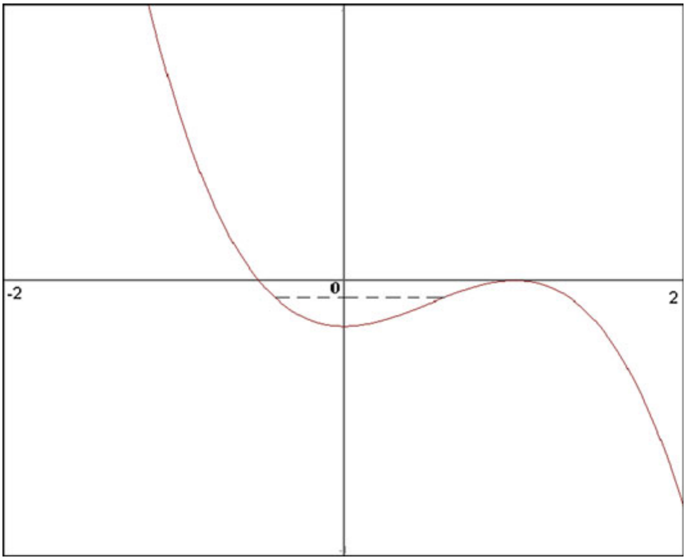

Fig. 3 Cubic potential

have multiple. The potential of Fig. 2 has 3 and that of Fig. 3 has 2. One of these multiple fixed points is a saddle. In Fig. 2 the fixed point $x = 0$ is the saddle and in Fig. 3 the saddle is $x = 1$. As argued in Strogatz [2] the time period goes to infinity when the homoclinic orbit is formed (starting and ending at the same fixed point) and from the general structure of the flow near a saddle it can be seen that the time period diverges logarithmically. In contrast, for the Morse potential, the saddle is at infinity.

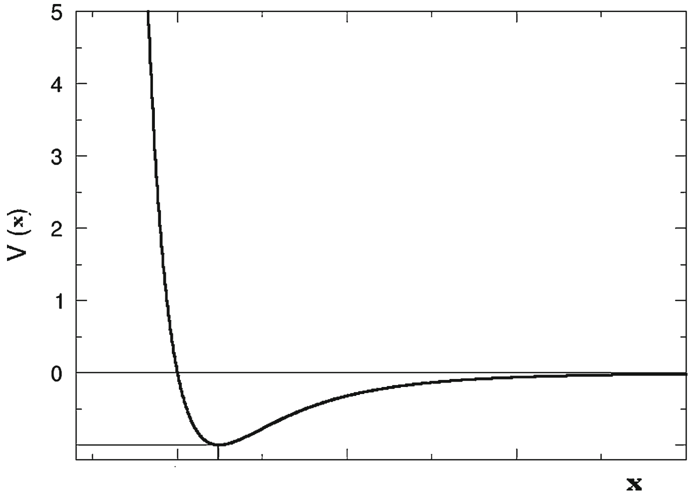

Fig. 4 Lennard Jones potential

The limiting trajectory i.e. the one for $E = 0$ is not a truly homoclinic orbit and hence the argument of Strogatz for the logarithmic divergence does not hold here. Is the behaviour shown in Eq.1.1 universal when there is only one equilibrium point?

Exact analytic forms for the time period are few and far between. Hence it would be nice to develop a perturbative method which can tackle potentials of the type shown in Fig. 1. We noted that the Lindstedt–Poincare procedure (hereafter referred to as LP) which is one of the most useful tools for analysing nonlinear oscillations has never been used for oscillations of the kind shown in Fig. 1. In recent years [3–10], LP has often been used for developing efficient numeric methods for studying anharmonic oscillators (quartic, cubic etc). We decided to use the traditional LP but widen its scope to include potentials of the kind shown in Fig. 1. Further we augmented it by including certain asymptotic behaviour to include potentials of the Lennard-Jones variety. It should be noted that for oscillations of Figs. 2 and 3 the LP method is not applicable for E approximately zero because of homoclinic orbit at $E = 0$. Here we explore first the LP method for the Morse oscillator. To our surprise we find that at every order it reproduces the exact answer of Eq. 1.1. Emboldened by this we try the same technique on a class of potentials similar to the one shown in Fig. 1. A typical member of this class is the Lennard-Jones potential—an attraction $1/x^6$ at large distances and repulsion $1/x^{12}$ at short distances. This is a potential which gives a good account of the force between two gas molecules. The potential can be written as $V = V_0 \left[\left(\frac{a}{x}\right)^{12} - \left(\frac{a}{x}\right)^6 \right]$. In the above V_0 is the strength of the potential and 'a' is a distance scale. The potential is sketched in Fig. 4.

The similarity with Fig. 1 is obvious. There will be bounded oscillatory motion for $E < 0$ as $E \rightarrow 0$ the time period will diverge. Will the divergence follow a $-E^{-1/2}$ behaviour as found for the Morse oscillator? We will show that for the class of potentials where the exponent 6 of the Lennard Jones is replaced by n and the 12 by 2n the divergence as $E \rightarrow 0$ is governed by an exponent which is a continuous function of

n. If n goes to infinity we get the result of the Morse potential where the divergence occurs with an exponent 1/2. Indeed this is expected because in the Morse potential the approach to V = 0 as x goes to infinity is exponentially fast which is faster than the power law approach of the generalised Lennard Jones form. Hence the Morse potential is the $n = \infty$ limit of the generalized Lennard Jones potential. This would imply that for any potential with an exponentially fast approach to zero, the divergence should occur with exponent 1/2. We test this out with the potential $V(x) = -V_0/\cosh^2(x/a)$ and find that indeed in this case the divergence occurs with exponent 1/2. The divergent behaviour as $E \to 0$ can be combined with LP to give interpolation formulae which give accurate values of time period for all values of E. The interpolation formula can be exact for certain types of potentials. This formula serves another very useful purpose. It allows us to connect with the corresponding quantum mechanical problem. Once T(E) is known the action can be found as

$$J(E) = \int T(E)dE + \text{constant} \tag{1.1}$$

The constant can be found by a direct evaluation of J(0). Once J(E) is known the Bohr Sommerfeld criterion gives the energy eigenvalues through the condition

$J(E) = (n + \alpha)h$, where α is a constant. For a one dimensional potential with two turning points, $\alpha = 1/2$.

In Sect. 2 we extend LP to the Morse oscillator and in Sect. 3 to the Lennard Jones class of potentials. A brief conclusion is given in Sect. 4.

2 Lindstedt Poincare technique and the Morse oscillator

In this section we apply the Lindstedt Poincare technique (LP) to the Morse oscillator whose potential we write as

$$V(x) = V_0 \left(1 - e^{-ax}\right)^2 \tag{2.1}$$

The energy E' of this potential is simply related to the energy E of the potential of Fig. 1 by the relation $E' = E + V_0$. To apply LP we expand the potential of Eq. (2.1) as

$$\begin{aligned} V(x) &= V_0 \left(ax - \frac{a^2x^2}{2} + \frac{a^3x^3}{6} - \frac{a^4x^4}{24} + \cdots\right)^2 \\ &= a^2x^2 \left(1 - ax + \frac{7a^2x^2}{12} - \frac{a^3x^3}{4} + \frac{31a^4x^4}{360} + \cdots\right) \end{aligned} \tag{2.2}$$

Treating a as a small parameter this would entail working to $O(a^4)$ in perturbation theory the equation of motion can be written as

$$\ddot{x} + 2V_0a^2x = 3V_0a^{36}x^2 - \frac{7}{3}V_0a^4x^3 + \frac{5}{4}V_0a^5x^4 - \frac{31}{60}V_0a^6x^5 + \cdots \tag{2.3}$$

We can scale the time by $\left(2V_0a^2\right)^{1/2}$ i.e. define $\tau = \left(2V_0a^2\right)^{1/2} t$ to write

$$\frac{d^2x}{d\tau^2} + x = \frac{3}{2}ax^2 - \frac{7}{6}a^2x^3 + \frac{5}{8}a^3x^4 - \frac{31}{120}a^4x^5 \tag{2.4}$$

Using a as the perturbation parameter, expanding

$$x = x_0 + ax_1 + a^2x_2 + a^3x_3 \tag{2.5}$$

and introducing the dressed frequency Ω such that

$$\Omega^2 = 1 + a\,\omega_1^2 + a^2\,\omega_2^2 + a^3\,\omega_3^2 + \cdots \tag{2.6}$$

one arrives at

$$\begin{aligned}\frac{d^2x}{d\tau^2} + \Omega^2x = {}& \frac{3}{2}ax^2 - \frac{7}{6}a^2x^3 + \frac{5}{8}a^3x^4 \\ & - \frac{31}{120}a^4x^5 + \cdots + (a\,\omega_1^2 + a^2\,\omega_2^2 + a^3\,\omega_3^2 + \cdots)x\end{aligned} \tag{2.7}$$

and at different orders of a the equations

$$\frac{d^2x_0}{d\tau^2} + \Omega^2x_0 = 0 \tag{2.8a}$$

$$\frac{d^2x_1}{d\tau^2} + \Omega^2x_1 = \frac{3}{2}x_0^2 + \omega_1^2\,x_0 \tag{2.8b}$$

$$\frac{d^2x_2}{d\tau^2} + \Omega^2x_2 = 3x_0x_1 - \frac{7}{6}x_0^3 + \omega_1^2\,x_1 + \omega_2^2\,x_0 \tag{2.8c}$$

$$\frac{d^2x_3}{d\tau^2} + \Omega^2x_3 = \frac{3}{2}(x_1^2 + 2x_0x_2) - \frac{7}{2}x_0^2x_1 + \frac{5}{8}x_0^4 + \omega_1^2\,x_2 + \omega_2^2\,x_1 + \omega_3^2\,x_0 \tag{2.8d}$$

$$\begin{aligned}\frac{d^2x_4}{d\tau^2} + \Omega^2x_4 = {}& 3(x_0x_3 + x_1x_2) - \frac{7}{6}(3x_0^2x_2 + 3x_0x_1^2) + \frac{5}{2}x_0^3x_1 - \frac{31}{120}x_0^5 + \omega_1^2\,x_3 \\ & + \omega_2^2\,x_2 + \omega_3^2\,x_1 + \omega_4^2\,x_0\end{aligned} \tag{2.8e}$$

We employ the initial conditions $x(t = 0) = A$ and $\dot{x}(t = 0) = 0$. Writing the solution of Eq. (2.8a) as

$$x_0 = A\cos\Omega t \tag{2.9}$$

all the subsequent equations have to be solved under the initial conditions $x_n(0) = \dot{x}_n(0) = 0$. We now work out Eq. (2.8b) as

$$\frac{d^2x_1}{d\tau^2} + \Omega^2x_1 = \frac{3A^2}{4}(1 + \cos 2\Omega t) + \omega_1^2\,A\cos\Omega t \tag{2.10}$$

The central point of LP is to remove the secular terms i.e. the resonance producing terms from the right hand side of the equation $\ddot{x}_n + \Omega^2 x_n = F_n(t)$ by a proper choice of ω_n^2. In this case of x1 the only secular term on the r.h.s. is $\omega_1^2 A \cos \Omega t$ and it is removed by setting $\omega_1^2 = 0$ which keeps $\Omega^2 = 1$ at this order. The solution for x_1 can now be written as

$$x_1 = \frac{3}{4}A^2 - \frac{1}{4}A^2 \cos 2\Omega t - \frac{1}{2}A^2 \cos \Omega t \tag{2.12}$$

We now explore Eq. (2.8c) and write

$$\begin{aligned}\frac{d^2x^2}{d\tau^2} + \Omega^2 x_2 = &-\frac{3}{4}A^3 \cos \Omega t + A^3 \cos \Omega t - \frac{3}{4}A^3 \cos 2\Omega t \\ &-\frac{2}{3}A^3 \cos 3\Omega t + \omega_2^2 A \cos \Omega t\end{aligned} \tag{2.13}$$

Removal of secular terms on the r.h.s. of Eq. (2.13) requires

$$\omega_2 = -A^2 \tag{2.14}$$

At this order the frequency of oscillations is given by

$$\Omega^2 = 1 - A^2 a^2 \tag{2.15}$$

In terms of the amplitude A the energy of motion can be written as

$$\begin{aligned}E' &= V(A) \\ &= a^2 A^2 \left[1 - aA + \frac{7}{12}a^2 A^2 + \cdots\right]\end{aligned} \tag{2.16}$$

Working to $O(a^2)$ we see that $E' = V_0 a^2 A^2$ and hence Eq. (2.15) can be written as

$$\Omega^2 = 1 - \frac{E'}{V_0} = -\frac{E}{V_0} \tag{2.17}$$

The solution for x_2 at this order can be written down from Eq. (2.13) as

$$x_2 = -\frac{3}{4}A^3 + \frac{1}{4}A^3 \cos 2\Omega t + \frac{1}{12}A^3 \cos 3\Omega t + \frac{5}{12}A^3 \cos \Omega t \tag{2.18}$$

We now obtain from Eq. (2.8d)

$$\begin{aligned}\frac{d^2x_3}{d\tau^2} + \Omega^2 x_3 = A^4 &\left[\frac{3}{32} - \cos \Omega t + \frac{1}{16}\cos 2\Omega t + \cos 3\Omega t + \frac{15}{32}\cos 4\Omega t\right] \\ &+\omega_3^2 A \cos \Omega t\end{aligned} \tag{2.19}$$

The removal of resonance term requires $\omega_3^2 = A^3$ (2.20)

At this order the frequency becomes

$$\Omega^2 = 1 - a^2A^2(1 - aA) \tag{2.21}$$

At the same order the energy E' would be given by $E' = V_0a^2A^2(1 - aA)$ and thus to this order we again recover from Eq. (2.21)

$$\Omega^2 - 1 - \frac{E'}{V_0} = -\frac{E}{V_0} \tag{2.22}$$

We can now write down x_3 as

$$x_3 = A^4\left[\frac{3}{32} - \frac{1}{48}\cos 2\Omega t - \frac{1}{8}\cos 3\Omega t - \frac{1}{32}\cos 4\Omega t + \frac{1}{12}\cos \Omega t\right] \tag{2.23}$$

Long and tedious algebra involving Eq. (2.8e) again leads to $\Omega^2 = -E/V_0$. Thus at every order in the LP we get the dimensional frequency as

$$\omega = a\sqrt{-2E} \tag{2.24}$$

which is the exact answer.

3 Lindstedt Poincare technique and the Lennard-Jones class of potentials

Having seen the effectiveness of Lindstedt–Poincare technique for a Morse oscillator in the previous section we now try it out on a class of potentials of similar shape, namely

$$V(x) = V_0\left[(a/x)^{2n} - (a/x)^n\right] \tag{3.1}$$

where n is a positive number. The dimensional constants V_0 and a set the scales for the energy and the distance respectively. For $n = 1$ we have a Coulomb attraction with a short range repulsion while for $n = 6$ we have the well known Lennard-Jones potential. Oscillatory motion will exist in this potential for $E < 0$. The minimum of this potential is at $x = x_0$ obtained from

$$2(a/x_0)^n = 1 \tag{3.2}$$

We expand about the minimum writing $x = x_0 + y$ so that

$$\begin{aligned} E = -V_0/4 + V_0(n^2/4)(y/x_0)^2 - V_0[n^2(n+1)/4](y/x_0)^3 \\ +V_0[n(n+1)(7n^2+11n)/48](y/x_0)^4 \end{aligned} \tag{3.3}$$

Clearly the minimum possible value of E is $-V_0/4$ and hence oscillatory motion will occur in the range $-V_0/4 < E < 0$. As $E \to 0$ the frequency of the oscillations tends to zero. The energy expressed in terms of the amplitude A of the oscillations is

$$E = -V_0/4 + V_0(n^2/4)(A/x_0)^2 - V_0[n^2(n+1)/4](A/x_0)^3 \\ + V_0[n^2(n+1)(7n+11)/48](A/x_0)^4 \ldots \quad (3.4)$$

The equation of motion in terms of y is

$$d^2y/dt^2 + (n^2/2)(V_0/x_0^2)\, y = (3V_0/4)[n^2(n+1)/x_0](y/x_0)^2 \\ -(V_0/12)[n^2(n+1)(7n+11)/x_0](y/x_0)^3 \quad (3.5)$$

Defining the dimensionless variables

$$z = y/x_0 \\ \tau^2 = \left(n^2/2\right)\left(V_0/x_0^2\right) t^2 = n^2 V_0 2^{-2/n} t^2/2a^2 = t^2/\tau_0^2 \quad (3.6)$$

where $\tau_0 = \frac{2^{1/n+1/2}a}{n\sqrt{V_0}}$
we get

$$d^2z/d\tau^2 + z = 3/2\,(n+1)\,z^2 - 1/6\,(n+1)\,(7n+11)\;z^3 \quad (3.7)$$

The frequency correct to A^2 order, following the method of Sect. 2, is

$$\Omega^2 = 1 - \left\{5/6\left[9\,(n+1)^2/4\right] - 3/4\,[n\,(n+1)\,(7n+11)/6]\right\}\;A^2/x_0^2 \\ = 1 - \frac{4E'}{V_0}\left(1+\frac{1}{n}\right)\left(1+\frac{1}{2n}\right) \quad (3.8)$$

where $E' = E + V_0/4$.

We expect Ω to vanish at $E' = V_0/4$. Unlike the Morse oscillator we do not see that $\Omega^2 = 1 - 4E'/V_0$. We can however characterize the behaviour at $E' = V_0/4$ by

$$\Omega^2 = \Omega_0^2(1 - 4E'/V_0)^\beta \\ = \Omega_0^2\left[1 - 4\,\beta\,E'/V_0 + \text{ higher order in } E'/V_0\right] \quad (3.9)$$

where Ω_0 is a constant independent of E'.

Comparing with Eq.(3.8)

$$\beta = (1 + 1/n)\,(1 + 1/2n) \quad (3.10)$$

There is an obvious weakness in the above identification of β. The asymptotic form of Eq. (3.9) would be equally valid if

$$\Omega^2 = \Omega_0^2\,(-4E/V_0)^\beta\, f(E'/V_0) \quad (3.11)$$

where $f(E'/V_0)$ is some analytic function of E'/V_0 with the expansion

$$f(E'/V_0) = 1 + C_1(-4E'/V_0) + C_2(-4E'/V_0)^2 + \cdots \quad (3.12)$$

where the C_i's are constants. In this case the expansion around $E' = 0$ has the form

$$\Omega^2 = \Omega_0^2[1 - 4\beta E'/V_0 + C1(-4E'/V_0) + \cdots] \tag{3.13}$$

and leads to, on comparing with Eq. (3.8),

$$\beta + C_1 = (1 + 1/n)(1 + 1/2n) \tag{3.14}$$

Thus β can be identified with the form of Eq. (3.9) if $f(E'/V_0) = 1$ i.e. Ω^2 proportional to $(-E)^\beta$ is an exact answer for all E.

To explore what is known about the exact frequency we start from the general formula of obtaining the time period. This can be found from the energy conservation as (we take the mass to be unity)

$$\begin{aligned} E &= 1/2\,(dx/dt)^2 + V(x) \\ &= 1/2\,(dx/dt)^2 + V_0\left[(a/x)^{2n} - (a/x)^n\right] \\ \text{or, } dt &= \frac{dx}{\sqrt{\left\{2\left[E - V_0\,(a/x)^{2n} + V_0\,(a/x)^n\right]\right\}}} \end{aligned} \tag{3.15}$$

If x_1 and x_2 with $x_2 > x_1$ are the two turning points of the motion i.e. x_1 and x_2 are the positive real roots of

$$E = V_0[(a/x)^{2n} - (a/x)^n]$$

then the time period is

$$T = \sqrt{2}\int_{x_1}^{x_2} \frac{dx}{\sqrt{\left\{E - V_0\,(a/x)^{2n} + V_0\,(a/x)^n\right\}}} \tag{3.16}$$

Using the dimensionless variables $y = (a/x)^n$ and $E/V_0 = A$
we find

$$T = \frac{\sqrt{2}a}{n\sqrt{V_0}}\int_{y_2}^{y_1} \frac{dy}{y^{(n+1)/n}\sqrt{\left\{A - y^2 + y\right\}}} \tag{3.17}$$

where y_1 and y_2 are the roots of $A - y^2 + y = 0$ with $y_1 > y_2$. The roots are found to be

$$y_{1,2} = 1/2\left[1 \pm \sqrt{\{1 + 4A\}}\right]$$

Our interest is in the situation $E < 0$ and hence $A < 0$. As $A \to 0$ the two roots $y_{1,2}$ tend to 1 and $-A$ respectively. In this limit Eq. (3.17) acquires the approximate form

(we note that most of the integrand comes from $y \approx |A|$ and hence y^2 can be neglected in comparison to y)

$$\begin{aligned} T &= \frac{\sqrt{2}a}{n\sqrt{V_0}} \int_{|A|}^{1} \frac{dy}{y^{(n+1)/n}\sqrt{\{y-|A|\}}} \\ &= \frac{\sqrt{2}a}{n\sqrt{V_0}} \frac{1}{|A|^{1/2+1/n}} \int_{1}^{\infty} \frac{dz}{z^{(n+1)/n}\sqrt{\{z-1\}}} \end{aligned}$$

For $A \to 0$ we obtain

$$T = \pi \left(a/\sqrt{V_0}\right) \left({}^{1}/{}_{\sqrt{2}}\right) (V_0/-E)^{1/2+1/n} \tag{3.18}$$

For n = 1 the integral in Eq. 3.10 can be evaluated exactly and we get

$$T = \pi \left(a/\sqrt{V_0}\right) \left(1/\sqrt{2}\right) (-V_0/E)^{3/2} \tag{3.19}$$

The asymptotic from of Eq. (3.18) is in this case the exact result.

For the case of arbitrary n we note that $\beta = 1+2/n$. From the LP result we thus find

$$\begin{aligned} C_1 &= 1 + 3/2n + 1/2n^2 - 1 - 2/n \\ &= 1/2n\,(1/n - 1) \end{aligned} \tag{3.20}$$

As expected for n = 1, $C_1 = 0$ from the Lindstedt Poincare theory which in this case yields the exact answer.

Let us consider n = 1/2 which will turn out to be another solvable case. In this case $C_1 = 1$ from Eq. (3.20) and from Eq. (3.11)

$$\Omega = \Omega_0(-4E/V_0)^{5/2}(1 - 2E'/V_0 + \cdots)$$

Inverting to find the time period

$$\begin{aligned} T &= \tau_0(-V_0/4E)^{5/2}(1 + 2E'/V_0) \\ &= \tau_0'(-V_0/4E)^{5/2}\,(1 + 4/3\;E/V_0) \end{aligned} \tag{3.21}$$

Turning to Eq. (3.17) in this case the exact time period is

$$\begin{aligned} T &= 2\sqrt{2}\frac{a}{\sqrt{V_0}} \int_{y_2}^{y_1} \frac{dy}{y^3\sqrt{\{A - y^2 + y\}}} \\ &= \tau_0'(-V_0/4E)^{5/2}\,(1 + 4/3E/V_0) \end{aligned} \tag{3.22}$$

Amazingly enough, first order Lindstedt Poincare gives the correct answer.

We now turn to the well known Lennard Jones potential for which $n = 6$. This leads to $\beta = 4/3$ and $C_1 = -5/72$ and from Eq. 3.06A

$$\Omega = \Omega_0(-4E/V_0)^{2/3}\,[1 + 5/18\,(E/V_0 + 1/4) + \cdots]$$
$$= \Omega_0'(-4E/V_0)^{2/3}\,[1 + 20/77\;E/V_0] \quad (3.23)$$

The time period in this lowest order approximation is

$$T\; = \tau_0(-V_0/4E)^{2/3}/\,(1 + 20/77\;E/V_0)\,. \quad (3.24)$$

This formula matches the exact numerically evaluated answers to within 1% for all values of E.

4 Conclusion

For a variety of potentials like the Morse potential, the Lennard-Jones class of potentials etc, we have used LP, at times augmented with an asymptotic analysis for $E \to 0$, to find the time period T(E) of oscillatory motion as a function of the energy. Sometimes the result is exact as is the case for the Morse potential and sometimes numerically accurate as for the Lennard Jones potential. As explained on the introduction, knowing T(E) allows us to infer the energy eigenvalues from the Bohr Sommerfeld quantisation condition. For the Morse potential

$$\left(n + \frac{1}{2}\right) h = J(E) - J(0) - \frac{2\,\pi}{a}\sqrt{-2mE} = \left(n_0 + \frac{1}{2}\right) h - \frac{2\,\pi}{a}\sqrt{-2mE} \quad (4.1)$$

where J(0), found by direct evaluation, is such that $n_0 = \frac{\sqrt{2mV_0}}{\hbar a}$.

Inserting this in Eq. (4.1) one gets the exact bound state energies for the Morse potential. For the Lenard Jones potential, T(E) is an excellent approximation and it leads to

$$J(E) = J(0) + 2\,\pi\left(\frac{77}{20}\right)^{1/3}\left(\frac{72}{77}\right)\frac{\sqrt{V_0 a^2}}{2^{5/3}}\left[\frac{1}{3}\ln\frac{1-y}{\sqrt{1+y+y^2}} - \frac{1}{3}\tan^{-1}\frac{y\sqrt{3}}{y+2}\right] \quad (4.2)$$

where $y = \left(-\frac{20E}{77V_0}\right)^{1/3}$. Setting $J(E) = \left(n + \frac{1}{2}\right) h$ we can now get the energy levels by solving a transcendental equation. We get 5% accuracy for all n, $0 < n < 23$.

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