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Excited States of the Anharmonic Oscillator Potentials: Variational Method

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Abstract

We applied variational method to calculate the first eight eigenvalues of quartic and sextic anharmonic oscillator potentials. By choosing a set of sophisticated trial wave functions, applying the orthogonal conditions between the eigenstates, and with the help of Maple software packages, we found that theses eight eigenvalues accurate and agree well with those obtained from the Runge-Kutta numerical integration method.

I. Introduction

A one-dimensional bound state problem, such as solving the time-independent Schrödinger equation with given potential V(x),

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\,\psi, \tag{1}$$

is a major subject regularly presented in the introductory quantum mechanics course. In most cases, the potential $V(x)$ is the harmonic oscillator potential $\frac{1}{2}m\omega^2x^2$, where ω is the angular frequency, because its eigenvalues and eigenfunctions can be obtained analytically. On top of that the model can be applied in many different areas of physics to explain all kinds of periodic motions. But when we extend the potential to the anharmonic region such as adding a quartic (αx^4) and/or sextic (βx^6) potentials, where α and β are coupling constants, the analytic solutions are practically impossible to achieve. Usually, an approximation scheme such as a perturbation method is used to undertake the problems, and it is accomplished in an order-by-order fashion, hence tedious expansion is needed. Another alternative is the variational method, [1] an approach that can be stated in a simple fashion and easily implemented, but requires good guess of a trial wave function. However it is always taught in a rather routine manner, namely the examples used in most textbooks are familiar problems with known solutions, not to mention that several important advantages of using the method, such as attaining remarkable precision of the eigenvalues and generalization to the high excited states, are seldom demonstrated. Previously the variational method had been carried out on the same potentials and emphasis was made on different choices of trial wave functions [2]. Later more detailed investigation was carried out to illustrate that impressively accurate ground state and first excited state eigenvalues could be achieved by adding more parameters to two sets of properly selected trial wave functions [3]. In this work, we extend the experiences we gained from studying the harmonic oscillator potential and applied them to the excited states of anharmonic oscillator potentials, we demonstrated that with the properly chose wave functions and orthogonality requirements between them, we were able to achieve their accurate eigenvalues, and found that they agree well with those obtained from the numerical integration method.

II. Theory

The variational principle used in solving time-independent Schrödinger equation states: for a given Hamiltonian $\hat{H}$, the energy expectation value of any trial wave function ψ_{trial} we choose will always be greater than or equal to the true total ground state energy E_{tot}:

$$E_{\text{tot}} \leq \langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle . \qquad (2)$$

This theorem is proved elegantly in all the known textbooks by constructing the trial wave functions as the linear combinations of all the eigenstates. In fact, this principle can be extended to the higher excited states as long as the trial wave function is orthogonal to the previously determined ground state and lower excited states. The argument roughly goes like following: since all the eigenstates are orthogonal to each other, if the previously determined states are proved to be of lower energy, then the newly founded states can only be states with higher energies, i.e. excited states. Nevertheless we seldom find any examples in the commonly used textbooks demonstrate this particular application. Therefore, it is the purpose of this work that we implement this application by calculating the first few excited states of the x^4 and x^6 potentials.

First, we review the variational procedures frequently stated in the textbooks: We choose a trial wave function $\psi_{\text{trial}}(\alpha,\beta,\gamma,...)$, where α, β, γ… are the variational parameters. With it we then form the expectation value of the system's total energy;

$$\mathrm{E}_{\text{tot}} = \langle \mathrm{KE} \rangle + \langle \mathrm{PE} \rangle . \tag{3}$$

Then by differentiating the total energy with respect to all the variational parameters and simultaneously solve those equations (which may be nonlinear), we obtain the best set of parameters. Afterward we substitute the optimized parameters back into Eq. (3), and compute the total energy. In fact, these procedures can be applied to the first excited state especially when the potential is symmetrical, i.e. $V(x) = V(-x)$, because the ground state wave function is certainly an even function, the orthogonality condition precludes the same parity for the first excited state wave function, thus it has to be odd in parity. Based on the known spectrum of the harmonic oscillator potential, we are aware that the wave functions of a symmetric potential can be divided into two categories according to their parities: even and odd, which are orthogonal to each other. Furthermore since coefficients of the wave functions are so well arranged that they are also orthogonal with each other, and are also orthogonal to each other within the same groups. In addition, we notice that there are more nodes in the higher excited states. In fact the number of nodes is commensurate to the order of the excited states, starting from the nodeless ground state and one node first excited state. So far the spectra of the quartic and sextic anharmonic oscillator potentials are not known analytically, but it is reasonable to assume that they have the similar property as that of the harmonic oscillator potential. Accordingly we assume the two categories of wavefunctions as following: the first four eigenstates of even parity are,

$$\psi_0 = \exp\left(-a_0 x^2 - b_0 x^4\right), \tag{4}$$

$$\psi_2 = \left(1 - c_2 x^2\right)\exp\left(-a_2 x^2 - b_2 x^4\right), \tag{5}$$

$$\psi_4 = \left(1 - c_4 x^2 + d_4 x^4\right)\exp\left(-a_4 x^2 - b_4 x^4\right), \tag{6}$$

$$\psi_6 = \left(1 - c_6 x^2 + d_6 x^4 - e_6 x^6\right)\exp\left(-a_6 x^2 - b_6 x^4\right). \tag{7}$$

Then here are the first four eigenstates of odd parity,

$$\psi_1 = x\exp\left(-a_1 x^2 - b_1 x^4\right), \tag{8}$$

$$\psi_3 = \left(x - c_3 x^3\right)\exp\left(-a_3 x^2 - b_3 x^4\right), \tag{9}$$

$$\psi_5 = \left(x - c_5 x^3 + d_5 x^5\right)\exp\left(-a_5 x^2 - b_5 x^4\right), \tag{10}$$

$$\psi_7 = \left(x - c_7 x^3 + d_7 x^5 - e_7 x^7\right)\exp\left(-a_7 x^2 - b_7 x^4\right). \tag{11}$$

where a_i, b_i (i = 0..7), c_i (i = 2..7), d_i (i = 4..7), and e_i (i = 6..7) are parameters to be determined from energy optimization. Owing to the orthogonally condition, that is

$$\int \psi_i^* \psi_j dx = 0 \quad \text{if} \quad i \neq j, \tag{12}$$

thus we can see that they are not completely independent of each other. However, we have to compute them sequentially, just to obtain E_0 (the ground state energy) and E_1 (first excited state energy) by using the standard energy optimization scheme. Then we use the obtained values of a_0, b_0 and a_1, b_1 to optimize the eigenenergies of ψ_2 and ψ_3. Since we know that ψ_2 has to be orthogonal to ψ_0 and similar condition goes to ψ_3 and ψ_1, we obtained c_2 and c_3 as:

$$c_2 = \frac{\int_{-\infty}^{\infty} \exp\left[-(a_0 + a_2)x^2 - (b_0 + b_2)x^4\right]dx}{\int_{-\infty}^{\infty} x^2 \exp\left[-(a_0 + a_2)x^2 - (b_0 + b_2)x^4\right]dx}, \tag{13}$$

and

$$c_3 = \frac{\int_{-\infty}^{\infty} x^2 \exp\left[-(a_1 + a_3)x^2 - (b_1 + b_3)x^4\right]dx}{\int_{-\infty}^{\infty} x^4 \exp\left[-(a_1 + a_3)x^2 - (b_1 + b_3)x^4\right]dx}. \tag{14}$$

Given that the ground state and first excited wave functions are automatically orthogonal to each other, parameters a_0, b_0 and a_1, b_1 are computed independently. Hence, we only have to vary a_2, b_2, and a_3, b_3 during the optimization of E_2 (second excited state energy) and E_3.(third excited state energy) separately. After that, we proceed to ψ_4 and ψ_5, following the same orthogonality condition between them and the previous determined eigenstates, we express c_4, d_4 and c_5, d_5 as the solution of the following linear simultaneous equations:

$$\begin{cases} \alpha_{11}c_4 - \alpha_{12}d_4 = \alpha_{13} \\ \alpha_{21}c_4 - \alpha_{22}d_4 = \alpha_{23} \end{cases} \tag{15}$$

$$\begin{cases} \beta_{11}c_5 - \beta_{12}d_5 = \beta_{13} \\ \beta_{21}c_5 - \beta_{22}d_5 = \beta_{23} \end{cases} \tag{16}$$

where

$$\alpha_{11} = \int_{-\infty}^{\infty} x^2 \exp\left[-(a_0 + a_4)x^2 - (b_0 + b_4)x^4\right]dx\,, \tag{17}$$

$$\alpha_{12} = \int_{-\infty}^{\infty} x^4 \exp\left[-(a_0 + a_4)x^2 - (b_0 + b_4)x^4\right]dx\,, \tag{18}$$

$$\alpha_{13} = \int_{-\infty}^{\infty} \exp\left[-(a_0 + a_4)x^2 - (b_0 + b_4)x^4\right]dx\,, \tag{19}$$

$$\alpha_{21} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)x^2 \exp\left[-(a_2 + a_4)x^2 - (b_2 + b_4)x^4\right]dx\,, \tag{20}$$

$$\alpha_{22} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)x^4 \exp\left[-(a_2 + a_4)x^2 - (b_2 + b_4)x^4\right]dx\,, \tag{21}$$

$$\alpha_{23} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)\exp\left[-(a_2 + a_4)x^2 - (b_2 + b_4)x^4\right]dx\,, \tag{22}$$

$$\beta_{11} = \int_{-\infty}^{\infty} x^4 \exp\left[-(a_1 + a_5)x^2 - (b_1 + b_5)x^4\right]dx\,, \tag{23}$$

$$\beta_{12} = \int_{-\infty}^{\infty} x^6 \exp\left[-(a_1 + a_5)x^2 - (b_1 + b_5)x^4\right]dx\,, \tag{24}$$

$$\beta_{13} = \int_{-\infty}^{\infty} x^2 \exp\left[-(a_1 + a_5)x^2 - (b_1 + b_5)x^4\right]dx\,, \tag{25}$$

$$\beta_{21} = \int_{-\infty}^{\infty} \left(1 - c_3x^2\right)x^4 \exp\left[-(a_3 + a_5)x^2 - (b_3 + b_5)x^4\right]dx\,, \tag{26}$$

$$\beta_{22} = \int_{-\infty}^{\infty} \left(1 - c_3x^2\right)x^6 \exp\left[-(a_3 + a_5)x^2 - (b_3 + b_5)x^4\right]dx\,, \tag{27}$$

and

$$\beta_{23} = \int_{-\infty}^{\infty} \left(1 - c_3x^2\right)x^2 \exp\left[-(a_3 + a_5)x^2 - (b_3 + b_5)x^4\right]dx\,, \tag{28}$$

then we express them in terms of the 2x2 determinants;

$$c_4 = \frac{\begin{vmatrix} \alpha_{13} & -\alpha_{12} \\ \alpha_{23} & -\alpha_{22} \end{vmatrix}}{\begin{vmatrix} \alpha_{11} & -\alpha_{12} \\ \alpha_{12} & -\alpha_{22} \end{vmatrix}} \qquad d_4 = \frac{\begin{vmatrix} \alpha_{11} & \alpha_{13} \\ \alpha_{21} & \alpha_{23} \end{vmatrix}}{\begin{vmatrix} \alpha_{11} & -\alpha_{12} \\ \alpha_{12} & -\alpha_{22} \end{vmatrix}} \tag{29}$$

and

$$c_5 = \frac{\begin{vmatrix} \beta_{13} & -\beta_{12} \\ \beta_{23} & -\beta_{22} \end{vmatrix}}{\begin{vmatrix} \beta_{11} & -\beta_{12} \\ \beta_{12} & -\beta_{22} \end{vmatrix}} \qquad d_5 = \frac{\begin{vmatrix} \beta_{11} & \beta_{13} \\ \beta_{21} & \beta_{23} \end{vmatrix}}{\begin{vmatrix} \beta_{11} & -\beta_{12} \\ \beta_{12} & -\beta_{22} \end{vmatrix}} \tag{30}$$

Now we see that the optimization procedures of ψ_4 and ψ_5 involved only two independent parameters each; a_4, b_4, and a_5, b_5. Finally, following the same reasoning, those three coefficients, c_6, d_6, and e_6, and c_7, d_7, and e_7, in the wave functions, ψ_6 and ψ_7, can be expressed in terms of the 3x3 determinants. Since those expressions are lengthy, we present them in the appendix. Also the total energies calculated from those wave functions are tedious, yet the optimizations procedures are the same as those of the previous states.

One remark regarding a mathematical trick we used often: due to the choice of our trial wave functions, we frequently encounter a special integral [4, 5],

$$\int_{-\infty}^{\infty} \exp\left[-2ax^2 - 2bx^4\right]dx = \frac{1}{4}\sqrt{\frac{a}{b}}K_{\frac{1}{4}}\left(\frac{a^2}{4b}\right)\exp\left(\frac{a^2}{4b}\right) \tag{31),}$$

where $K_\sigma(z)$ is the modified Bessel function of fractional order σ. Based on that, we derived compact expressions for the following related integrals

$$\int_{-\infty}^{\infty} x^{2n} \exp\left[-ax^2 - bx^4\right]dx, \tag{32}$$

where n is a positive integer, by differentiating repetitively the right hand side of Eq. (31) with respect to a and/or b and making use of the Bessel function recursion relations [4]. Even though the total energy equations of the excited states are lengthy and complicated, since all the integrals are analytical, the entire computation was reasonably fast because we did not have to evaluate them numerically.

III. Results and discussion

In this section, we report the numerical results obtained from using the variational method. In each of the following tables 1 - 4 we present the essential variation parameters, namely the a_i and b_i, (i = 0. 1...7), the coefficients of the x^2 and x^4 terms in the trial wave functions, variational eigenvalues and compare them with those obtained from the Runge-Kutta numerical integration. As we notice that all the discrepancies are within 0.1 %, also the systematic change of a_i and b_i: that is all a_i are increasing and b_i are decreasing when progressing from low to high excited states that are more widespread. In addition, we only list a_i and b_i in the tables, because all the other parameters in the wave functions are derivable from them.

X^4 Eigenstates (even)

	Variational and	Numerical results
ψ_0, $a_0=0.545673$ $b_0=0.074277$	1.060450	1.060362
ψ_2,$a_2=0.728631$ $b_2=0.057914$	7.455914	7.455698
ψ_4, $a_4=0.844816$ $b_4=0.050574$	16.262280	16.261826
ψ_6, $a_6=0.935001$ $b_6=0.046006$	26.529053	26.528471

Table 1

X^4 Eigenstates (odd)

	Variational and	Numerical results
ψ_1, $a_1=0.652604$ $b_1=0.0638284$	3.799817	3.799673
ψ_3, $a_3=0.791054$ $b_3=0.0537548$	11.645050	11.644746
ψ_5, $a_5=0.892066$ $b_5=0.048099$	21.238893	21.238373
ψ_7, $a_7=0.987158$ $b_7=0.0425794$	32.100006	32.098598

Table 2

X^6 Eigenstates (even)

	Variational and	Numerical results
ψ_0, $a_0=0.531079$ $b_0=0.1774098$	1.145193	1.1448025
ψ_2, $a_2=0.788120$ $b_2=0.1738413$	9..074538	9.0730846
ψ_4, $a_4=0.996391$ $b_4=0.170359$	21.717409	21.714165
ψ_6, $a_6=1.174986$ $b_6=0.167198$	37.618765	37.613087

Table 3

X^6 Eigenstates (odd)

	Variational and	Numerical results
ψ_1, $a_1=0.661166$ $b_1=0.1769575$	4.339415	4.3385987
ψ_3, $a_3=0.897997$ $b_3=0.171806$	14.937455	14.935170
ψ_5, $a_5=1.086226$ $b_5=0.1692858$	29.304083	29.299646
ψ_7, $a_7=1.262520$ $b_7=0.164755$	46.602822	46.595212

Table 4

Next we display figures 1 – 4 to show the wave functions of these two potentials, we observe that even though they share the similar feature as that of the harmonic oscillator potential, yet we can distinguish them from their ranges, namely the spread of the x^4 potential wave functions are clearly wider than those of the x^6.

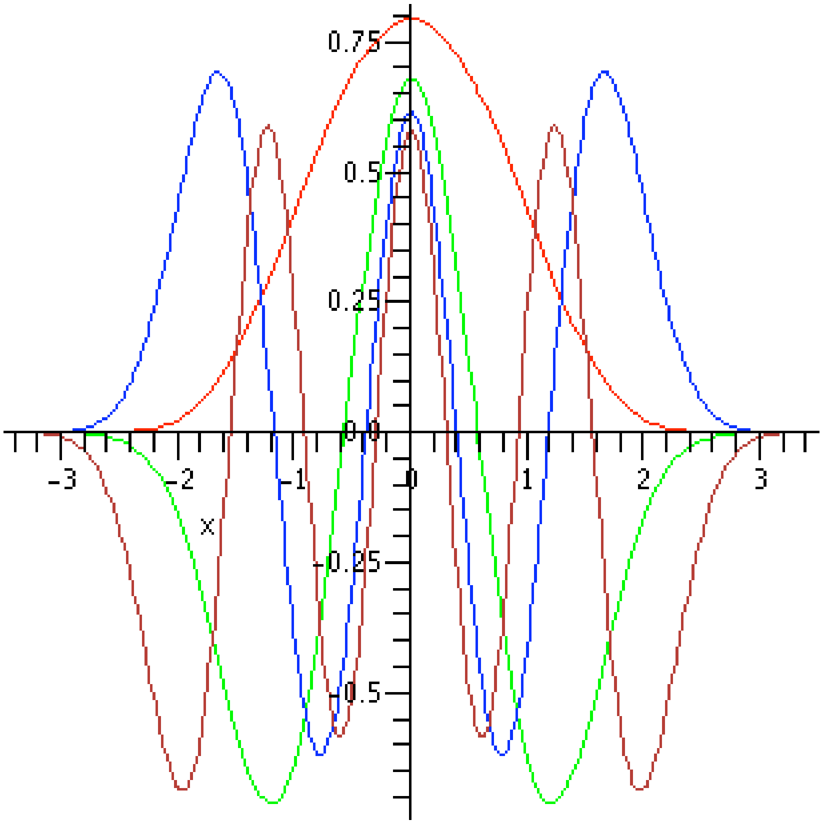

Figure 1. First four even parity eigenstates of the x^4 potential: ground state (red), second (blue), fourth (green) and sixth (brown) excited states.

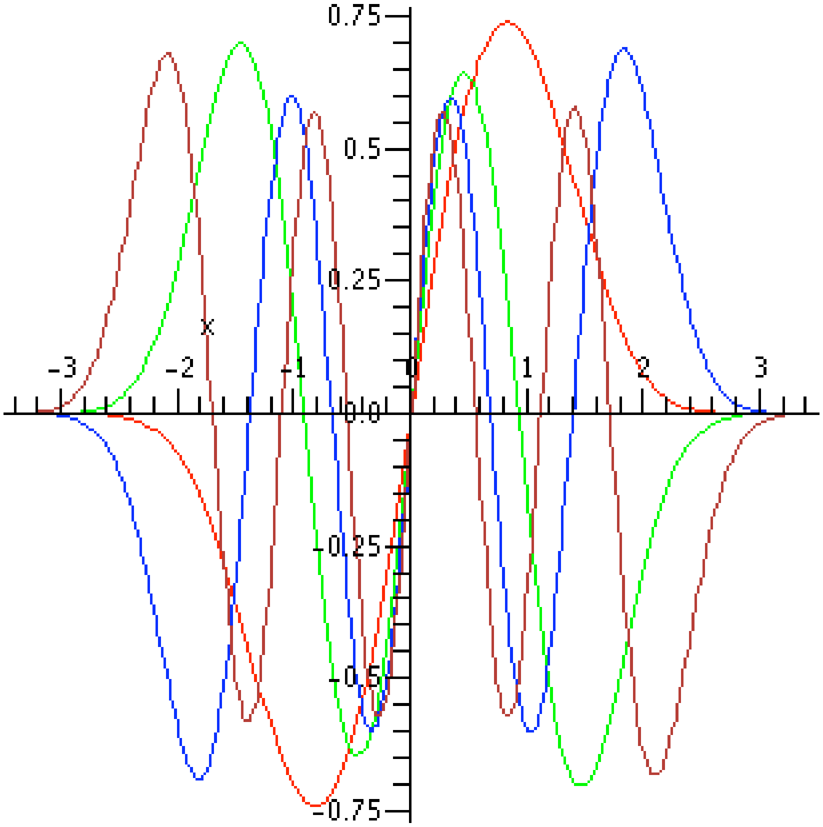

Figure 2. First four odd parity eigenstates of the x^4 potential: first (red), third (green), fifth (blue) and seventh (brown) excited states.

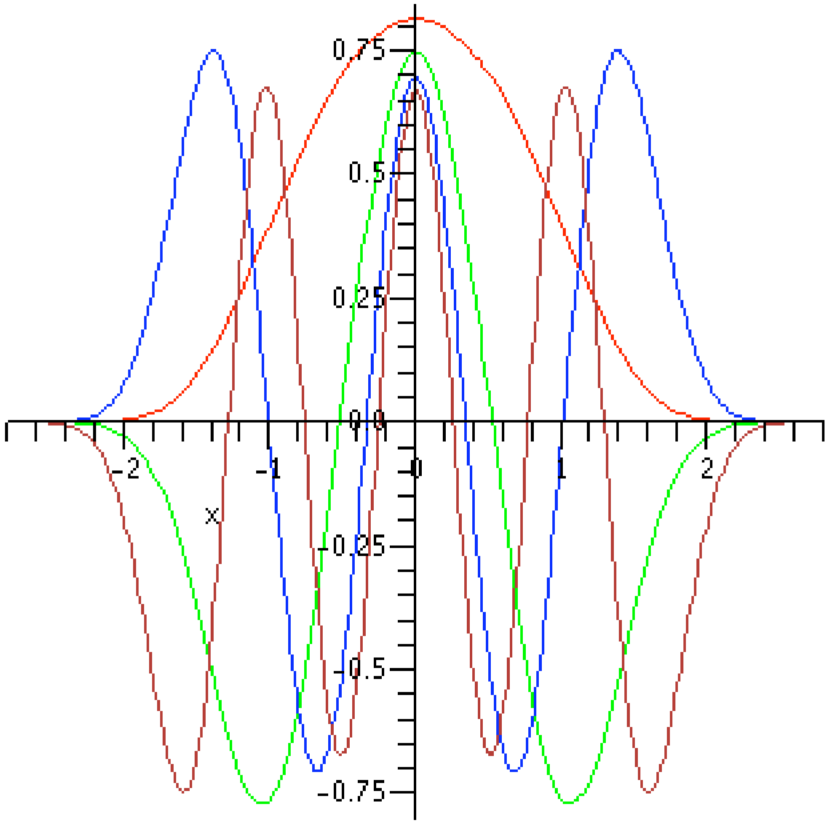

Figure 3. First four even parity eigenstates of the x^6 potential: ground state (red), second (green), fourth (blue) and sixth (brown) excited states.

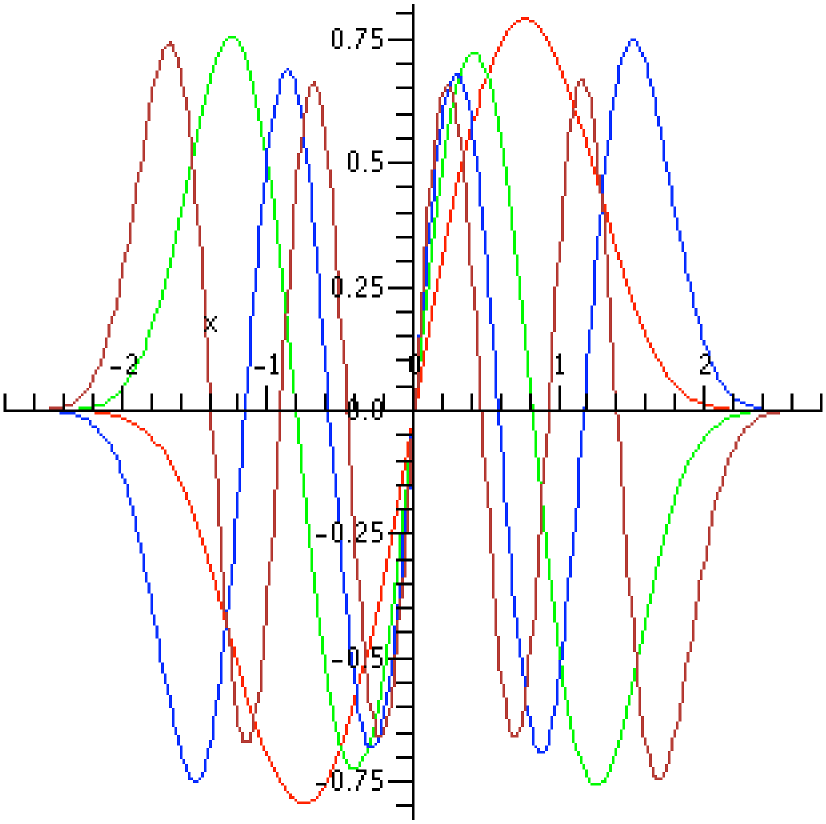

Figure 4. First four odd parity eigenstates of the x^6 potential: first (red), third (green), fifth (blue) and seventh (brown) excited states.

To conclude, two remarks regarding our numerical computation are in order: first, when carrying out the numerical calculation, for convenience we set 2m, the Planck's constant $\hbar$, and coupling constants of the potential in Eq. (1), α and β, equal to one. In fact, that is equivalent to transforming Eq. (1) to a dimensionless differential equation by using a simple scale transformation: i.e. when V(x) = αx^4, we convert it to

$$-\frac{d^2\psi}{dz^2}+z^4\psi=\varepsilon\psi \qquad (33),$$

by substituting $z=\left(\frac{\hbar^2}{2m\alpha}\right)^{1/6}x$ and $\varepsilon=\left(\frac{2m}{\hbar^2}\right)^{2/3}\frac{E}{\alpha^{1/3}}$, or when V(x) = βx^6, then we convert Eq. (1) to

$$-\frac{d^2\psi}{dz^2}+z^6\psi=\varepsilon\psi \qquad (34),$$

by substituting $z=\left(\frac{\hbar^2}{2m\beta}\right)^{1/8}x$ and $\varepsilon=\left(\frac{2m}{\hbar^2}\right)^{3/4}\frac{E}{\beta^{1/4}}$. Second, we used the Maple 10 to perform all the analytical and numerical calculations, our worksheets are available for the interested readers, please send request to the attached addresses.

V. Conclusion

In this work, we applied the variational method to the quartic and sextic anharmonic oscillator potentials: first we choose a set of trial wave functions from studying the spectrum of harmonic oscillator potential and require them to be orthogonal to each other, then we demonstrated not only could we achieve accurate ground and first excited state energies, but also those of the higher excited states agree well the numerical integration scheme. Nevertheless the procedures have to be performed consecutively. Also, while carrying out this project, we used Maple 10 packages intensively and found that it is a useful tool in manipulating lengthy equations and optimizing variational parameters in complex trial wave functions.

VI. Acknowledgements

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VII. Appendix

After we applied the orthogonality conditions, the coefficients, c_6, d_6, e_6, c_7, d_7, and e_7 in ψ_6 and ψ_7 are shown to be determined by the following linear simultaneous equations:

$$\begin{cases}\gamma_{11}c_6-\gamma_{12}d_6+\gamma_{13}e_6=\gamma_{14}\\ \gamma_{21}c_6-\gamma_{22}d_6+\gamma_{23}e_6=\gamma_{24}\\ \gamma_{31}c_6-\gamma_{32}d_6+\gamma_{33}e_6=\gamma_{34}\end{cases} \qquad (A1)$$

and

$$\begin{cases} \delta_{11}c_6 - \delta_{12}d_6 + \delta_{13}e_6 = \delta_{14} \\ \delta_{21}c_6 - \delta_{22}d_6 + \delta_{23}e_6 = \delta_{24} \\ \delta_{31}c_6 - \delta_{32}d_6 + \delta_{33}e_6 = \delta_{34} \end{cases} \qquad \text{(A2)}$$

where

$$\gamma_{11} = \int_{-\infty}^{\infty} x^2 \exp\left[-(a_0 + a_6)x^2 - (b_0 + b_6)x^4\right]dx \qquad \text{(A3)}$$

$$\gamma_{12} = \int_{-\infty}^{\infty} x^4 \exp\left[-(a_0 + a_6)x^2 - (b_0 + b_6)x^4\right]dx \qquad \text{(A4)}$$

$$\gamma_{13} = \int_{-\infty}^{\infty} x^6 \exp\left[-(a_0 + a_6)x^2 - (b_0 + b_6)x^4\right]dx \qquad \text{(A5)}$$

$$\gamma_{14} = \int_{-\infty}^{\infty} \exp\left[-(a_0 + a_6)x^2 - (b_0 + b_6)x^4\right]dx \qquad \text{(A6)}$$

$$\gamma_{21} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)x^2 \exp\left[-(a_2 + a_6)x^2 - (b_2 + b_6)x^4\right]dx \qquad \text{(A7)}$$

$$\gamma_{22} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)x^4 \exp\left[-(a_2 + a_6)x^2 - (b_2 + b_6)x^4\right]dx \qquad \text{(A8)}$$

$$\gamma_{23} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)x^6 \exp\left[-(a_2 + a_6)x^2 - (b_2 + b_6)x^4\right]dx \qquad \text{(A9)}$$

$$\gamma_{24} = \int_{-\infty}^{\infty} \left(1 - c_2x^2\right)\exp\left[-(a_2 + a_6)x^2 - (b_2 + b_6)x^4\right]dx \qquad \text{(A10)}$$

$$\gamma_{31} = \int_{-\infty}^{\infty} \left(1 - c_4x^2 + d_4x^4\right)x^2 \exp\left[-(a_4 + a_6)x^2 - (b_4 + b_6)x^4\right]dx \qquad \text{(A11)}$$

$$\gamma_{32} = \int_{-\infty}^{\infty} \left(1 - c_4x^2 + d_4x^4\right)x^4 \exp\left[-(a_4 + a_6)x^2 - (b_4 + b_6)x^4\right]dx \qquad \text{(A11)}$$

$$\gamma_{33} = \int_{-\infty}^{\infty} \left(1 - c_4x^2 + d_4x^4\right)x^6 \exp\left[-(a_4 + a_6)x^2 - (b_4 + b_6)x^4\right]dx \qquad \text{(A12)}$$

$$\gamma_{34} = \int_{-\infty}^{\infty} \left(1 - c_4x^2 + d_4x^4\right)\exp\left[-(a_4 + a_6)x^2 - (b_4 + b_6)x^4\right]dx \qquad \text{(A13)}$$

$$\delta_{11} = \int_{-\infty}^{\infty} x^4 \exp\left[-(a_1 + a_7)x^2 - (b_1 + b_7)x^4\right]dx \qquad \text{(A14)}$$

$$\delta_{12} = \int_{-\infty}^{\infty} x^6 \exp\left[-(a_1 + a_7)x^2 - (b_1 + b_7)x^4\right]dx \qquad \text{(A15)}$$

$$\delta_{13} = \int_{-\infty}^{\infty} x^8 \exp\left[-(a_1 + a_7)x^2 - (b_1 + b_7)x^4\right]dx \qquad \text{(A16)}$$

$$\delta_{14} = \int_{-\infty}^{\infty} x^2 \exp\left[-(a_1 + a_7)x^2 - (b_1 + b_7)x^4\right]dx \qquad \text{(A17)}$$

$$\delta_{21} = \int_{-\infty}^{\infty} \left(1 - c_3 x^2\right) x^4 \exp\left[-\left(a_3 + a_7\right)x^2 - \left(b_3 + b_7\right)x^4\right] dx \tag{A18}$$

$$\delta_{22} = \int_{-\infty}^{\infty} \left(1 - c_3 x^2\right) x^6 \exp\left[-\left(a_3 + a_7\right)x^2 - \left(b_3 + b_7\right)x^4\right] dx \tag{A19}$$

$$\delta_{23} = \int_{-\infty}^{\infty} \left(1 - c_3 x^2\right) x^8 \exp\left[-\left(a_3 + a_7\right)x^2 - \left(b_3 + b_7\right)x^4\right] dx \tag{A20}$$

$$\delta_{24} = \int_{-\infty}^{\infty} \left(1 - c_3 x^2\right) x^2 \exp\left[-\left(a_3 + a_7\right)x^2 - \left(b_3 + b_7\right)x^4\right] dx \tag{A21}$$

$$\delta_{31} = \int_{-\infty}^{\infty} \left(1 - c_5 x^2 + d_5 x^4\right) x^4 \exp\left[-\left(a_5 + a_7\right)x^2 - \left(b_5 + b_7\right)x^4\right] dx \tag{A22}$$

$$\delta_{32} = \int_{-\infty}^{\infty} \left(1 - c_5 x^2 + d_5 x^4\right) x^6 \exp\left[-\left(a_5 + a_7\right)x^2 - \left(b_5 + b_7\right)x^4\right] dx \tag{A23}$$

$$\delta_{33} = \int_{-\infty}^{\infty} \left(1 - c_5 x^2 + d_5 x^4\right) x^8 \exp\left[-\left(a_5 + a_7\right)x^2 - \left(b_5 + b_7\right)x^4\right] dx \tag{A24}$$

$$\delta_{34} = \int_{-\infty}^{\infty} \left(1 - c_5 x^2 + d_5 x^4\right) x^2 \exp\left[-\left(a_5 + a_7\right)x^2 - \left(b_5 + b_7\right)x^4\right] dx \tag{A25}$$

then we can express them in terms of the 3x3 determinants:

$$c_6 = \frac{\begin{vmatrix} \gamma_{14} & -\gamma_{12} & \gamma_{13} \\ \gamma_{24} & -\gamma_{22} & \gamma_{23} \\ \gamma_{34} & -\gamma_{32} & \gamma_{33} \end{vmatrix}}{\begin{vmatrix} \gamma_{11} & -\gamma_{12} & \gamma_{13} \\ \gamma_{21} & -\gamma_{22} & \gamma_{23} \\ \gamma_{31} & -\gamma_{32} & \gamma_{33} \end{vmatrix}}, \quad d_6 = \frac{\begin{vmatrix} \gamma_{11} & \gamma_{14} & \gamma_{13} \\ \gamma_{21} & \gamma_{24} & \gamma_{23} \\ \gamma_{31} & \gamma_{34} & \gamma_{33} \end{vmatrix}}{\begin{vmatrix} \gamma_{11} & -\gamma_{12} & \gamma_{13} \\ \gamma_{21} & -\gamma_{22} & \gamma_{23} \\ \gamma_{31} & -\gamma_{32} & \gamma_{33} \end{vmatrix}}, \quad \text{and } e_6 = \frac{\begin{vmatrix} \gamma_{11} & -\gamma_{12} & \gamma_{14} \\ \gamma_{21} & -\gamma_{22} & \gamma_{24} \\ \gamma_{31} & -\gamma_{32} & \gamma_{34} \end{vmatrix}}{\begin{vmatrix} \gamma_{11} & -\gamma_{12} & \gamma_{13} \\ \gamma_{21} & -\gamma_{22} & \gamma_{23} \\ \gamma_{31} & -\gamma_{32} & \gamma_{33} \end{vmatrix}} \tag{A26}$$

and

$$c_7 = \frac{\begin{vmatrix} \delta_{14} & -\delta_{12} & \delta_{13} \\ \delta_{24} & -\delta_{22} & \delta_{23} \\ \delta_{34} & -\delta_{32} & \delta_{33} \end{vmatrix}}{\begin{vmatrix} \delta_{11} & -\delta_{12} & \delta_{13} \\ \delta_{21} & -\delta_{22} & \delta_{23} \\ \delta_{31} & -\delta_{32} & \delta_{33} \end{vmatrix}}, \quad d_7 = \frac{\begin{vmatrix} \delta_{11} & \delta_{14} & \delta_{13} \\ \delta_{21} & \delta_{24} & \delta_{23} \\ \delta_{31} & \delta_{34} & \delta_{33} \end{vmatrix}}{\begin{vmatrix} \delta_{11} & -\delta_{12} & \delta_{13} \\ \delta_{21} & -\delta_{22} & \delta_{23} \\ \delta_{31} & -\delta_{32} & \delta_{33} \end{vmatrix}}, \quad \text{and } e_7 = \frac{\begin{vmatrix} \delta_{11} & -\delta_{12} & \delta_{14} \\ \delta_{21} & -\delta_{22} & \delta_{24} \\ \delta_{31} & -\delta_{32} & \delta_{34} \end{vmatrix}}{\begin{vmatrix} \delta_{11} & -\delta_{12} & \delta_{13} \\ \delta_{21} & -\delta_{22} & \delta_{23} \\ \delta_{31} & -\delta_{32} & \delta_{33} \end{vmatrix}} \tag{A27}$$

Now we notice that all the coefficients in ψ_6 and ψ_7 are dependent on the parameters in the previous eigenstates and only a_6, b_6, a_7, and b_7 have to be calculated from the variational procedures.

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Systematic Convergence in Applying the Variational Method to Anharmonic Oscillator Potentials

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Abstract

We applied the variational method to determine the ground and first excited state energies of quartic and sextic anharmonic oscillator potentials. Starting from two sets of trial wave functions, we showed that by introducing additional terms, the energy eigenvalues gradually converge to those obtained from the Runge-Kutta numerical integration method.

I. Introduction

In a one-dimensional quantum mechanics bound state problem, we have to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad (1)$$

where V(x) is the potential of the system. In most textbooks, the harmonic oscillator potential $\frac{1}{2}kx^2$, where k is the force constant of the spring, is used as an example from which eigenvalues and eigenfunctions can be obtained analytically in an elegant manner. But when we extend to the anharmonic regions: that is using quartic (αx^4) and sextic (βx^6) potentials, where α and β are coupling constants, analytic solutions are practically impossible to attain. Usually, methods such as the Runge-Kutta integration scheme can be used to calculate the bound state eigen-energies and functions, but the results can only be tabulated numerically. However, there are other alternatives to obtain analytical solutions: the variational method, which is simple in principle but sometimes not easy to implement, can be applied to many problems of this kind. By reviewing cases in either textbooks or literature, we notice that in order to achieve a good result, one must rely on physical intuition to guess an accurate trial wave function. At the same time the function must be manageable by sound mathematical skill. In spite of the many triumphant cases, such as the helium atom and hydrogen molecule, difficulties in improving the result still exist. This is because one usually has to include many additional terms in the trial wave function to obtain smaller corrections that can sometimes make the calculations rather complicated. In this work, we achieved numerical accuracy for the ground and first excited state energies of the anharmonic oscillator potentials down to six significant figures by using two different trial wave functions and systematically including additional terms.

II. Theory

The variational principle used in solving time-independent Schrödinger equation states as following: for a given Hamiltonian $\hat{\mathrm{H}}$, the energy expectation value of any trial wave function ψ_{trial} we choose will always be greater than or equal to the true total ground state energy $\mathrm{E}_{\mathrm{tot}}$:

$$\mathrm{E}_{\mathrm{tot}} \leq \left\langle \psi_{\mathrm{trial}} \middle| \hat{\mathrm{H}} \middle| \psi_{\mathrm{trial}} \right\rangle, \qquad (2)$$

where ψ_{trial} is a trial wave function, when we happen to choose the true wave function (*1*). In fact, this principle can be extended to the excited states as well, as long as the trial wave function is orthogonal to the previously determined ground state and excited state wave functions. This point is demonstrated in many commonly used Quantum Mechanics textbooks by using an elegant proof that ψ_{trial} is expressed as a linear combination of all the eigenfunctions of $\hat{\mathrm{H}}$, which is analogous to that of the Fourier expansion.

Now let us briefly review the variational procedure: first, we calculate the total energy expectation value, which is the sum of potential and kinetic energies.

$$\mathrm{E}_{\mathrm{tot}} = \left\langle \mathrm{KE} \right\rangle + \left\langle \mathrm{PE} \right\rangle \qquad (3)$$

Second, we minimize the total energy to obtain the best set of parameters. We do this by differentiating the total energy with respect to all the variational parameters and simultaneously solve the equations, which may be nonlinear. Then we substitute the optimized parameters back to Eq. (3) to deduce the total energy. Finally, a useful way to evaluate the trial wave function is to compare the effective potential defined as:

$$V_{\mathrm{eff}} = E + \frac{\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}{\psi} \qquad (4),$$

with the actual potential V(x), hence there will be a perfect match if the trial wave function agrees well with the exact solution.

In this project we applied the variational principle to two anharmonic potentials: x^4 and x^6, similar study has been carried out before *(2)*, in which different set of trial wave functions were used to calculate the ground state and first excited state energies. Some of the values so obtained were accurate to within few percent of those computed from using numerical integration schemes. When selecting the trial wave functions, it helps to look at the graph, Figure 1. of anharmonic potentials mentioned above and the well-known harmonic oscillator potential,

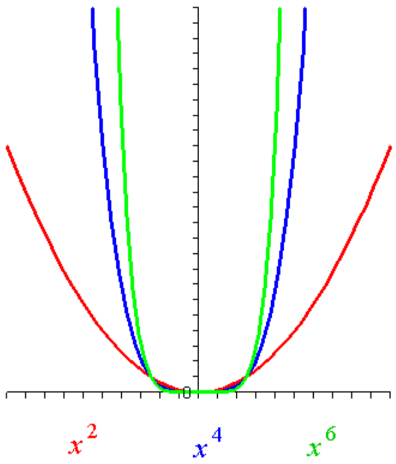

Figure 1.

Since the solution of the x^2 potential is known to be Gaussian-like i.e. e^{-ax^2}, a natural choice for the steeper potential would be e^{-ax^2} (*Trial Wave Function 1*), because it is symmetrical, i.e. $\psi(x) = \psi(-x)$, more localized and decays faster than the Gaussians.

As we carried out the standard variational procedure on ground and first excited states of both x^4 and x^6 potentials, we obtained results in the neighborhood of 6-13% accuracy of the numerical integration, i.e. the Runge-Kutta method (*results obtained separately)* These results are good enough for demonstration, but maximum accuracy can still be reached.

Based on previous experience we know we can add on more terms to the trial wave function to increase the accuracy of the energy eigenvalues. The simplest way we can do this is to multiply the original wave function by a $\left(1-\left(\frac{x}{b}\right)^2\right)$ term. This preserves the symmetry, and slightly modifies the behavior near the origin. In Figure 2 it is shown how this correction term slightly modifies the function, but only near the center because as x gets larger the exponential will dominate.

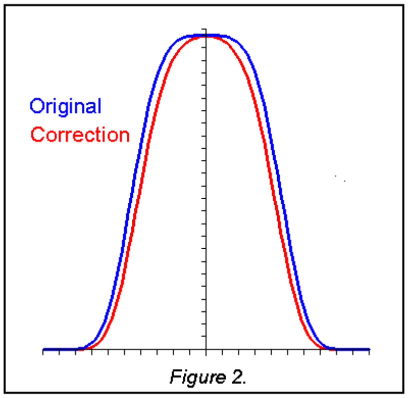

Figure 2.

Adding just one correction in refines the accuracy down to about 3-6%. To make further refinements we systematically add more terms with increasing order of x, such as:

$$1-\left(\frac{x}{b}\right)^2+\left(\frac{x}{c}\right)^4-\left(\frac{x}{d}\right)^6+\left(\frac{x}{e}\right)^8-\left(\frac{x}{f}\right)^{10}+\left(\frac{x}{g}\right)^{12}-\left(\frac{x}{h}\right)^{14}+\left(\frac{x}{i}\right)^{16}\cdots \qquad (5)$$

where a, b, c…i are variational parameters that we included progressively. We observed that after the fourth term the accuracy is high but the convergence is slow. By the time we reached respectively the 7th and 9th term for the x^4 and x^6 potentials, we match the numerical results down to the 6th significant figure. All the above calculations were performed using Maple 9.5 initially.

Adding more correction terms was an effective way of getting better energy values, but we can also pick a more sophisticated trial wave function such as $e^{-ax^2-bx^4}$ (*Trial Wave Function 2*). This is because it merges the feature of the Gaussian with our previous trial wave function. This gives us better control of the asymptotic behavior with two parameters in the exponent. Carrying out the variational procedures on this trial wave function gives us accuracy of less then 0.1%, but utilizing the second trial wave function requires *a prior* knowledge of the integral (*3*) and Bessel functions (*4*), which renders more complex manipulations. The high level of accuracy obtained is because the Gaussian factor e^{-ax^2} contains most of the correction terms that we added to the first trial wave function, Eq. (5), this can be verified by comparing them with the Taylor expansion the Gaussian term. We can still add in more correction terms, as we did in the first case, but our initial result is already matched closely. Therefore, it requires less terms to reach similar high precision. Furthermore, all the above arguments can be applied to the first excited state by multiplying an extra factor x in front of the equations (5), because its wave function is antisymmetrical, that is $\psi(x) = -\psi(-x)$.

III. Results and Discussion

In this section, we present in detail the results obtained from the variational method. In each of the following tables 1-4 and figures 3-4, we show the variational results compared with the numerically estimated values obtained by using the Runge-Kutta numerical integration method tabulated in Ref. (*2*). As we can see the initial result of the first trial wave function is barely acceptable, but after including just one parameter the level of accuracy doubles. When we include 6-7 coefficients, the result converges to the numerical values. The second trial wave function started with satisfactory accuracy, when 4 more coefficients are added, the result matches the numbers precisely. Using the updated Maple 10 we performed all the analytical and numerical calculations. When the number of variational parameters is small, such as less than 5 to 6, we obtained the answers very quickly, but as we included more parameters in the trial wave functions, the calculations became lengthy, and we had to set the initial values near the previous results, nevertheless the improvement is minute. Therefore, we believe our work reached the current limit of the multi-dimensional optimization programs, and it is necessary to increase their capability to improve the accuracy.

x^4 Ground State

Numerical result: 1.0603621

Trial Function 1

# of Coefficients	Energy Value	% Discrepancy
1	1.2016110	13.32%
2	1.1213082	5.75%
7	1.0603621	0.00%

Trial Function 2

# of Coefficients	Energy Value	% Discrepancy
2	1.0604498	0.00827%
3	1.0603639	0.000076%
6	1.0603621	0.00%

Table 1

x^4 First Excited State

Numerical result: 3.7996730

Trial Function 1

# of Coefficients	Energy Value	% Discrepancy
1	4.1063870	8.07%
2	3.9880590	4.96%
8	3.7996730	0.00%

Trial Function 2

# of Coefficients	Energy Value	% Discrepancy
2	3.7998168	0.00379%
3	3.7996747	0.000045%
6	3.7996730	0.00%

Table 2

x^6 Ground State

Numerical result:1.1448025

Trial Function 1

# of Coefficients	Energy Value	% Discrepancy
1	1.2581373	9.89%
2	1.1818932	3.24%
9	1.1448025	0.00%

Trial Function 2

# of Coefficients	Energy Value	% Discrepancy
2	1.1451929	.034%
3	1.1449384	0.0119%
6	1.1448025	0.00%

Table 3

x^6 First Excited State

Numerical result: 4.3385987

Trial Function 1

# of Coefficients	Energy Value	% Discrepancy
1	4.5889291	5.97%
2	4.4687589	3.00%
9	4.3385990	0.000%

Trial Function 2

# of Coefficients	Energy	% Discrepancy
2	4.3394151	0.0188%
3	4.3388517	0.00583%
6	4.3385988	0.00%

Table 4

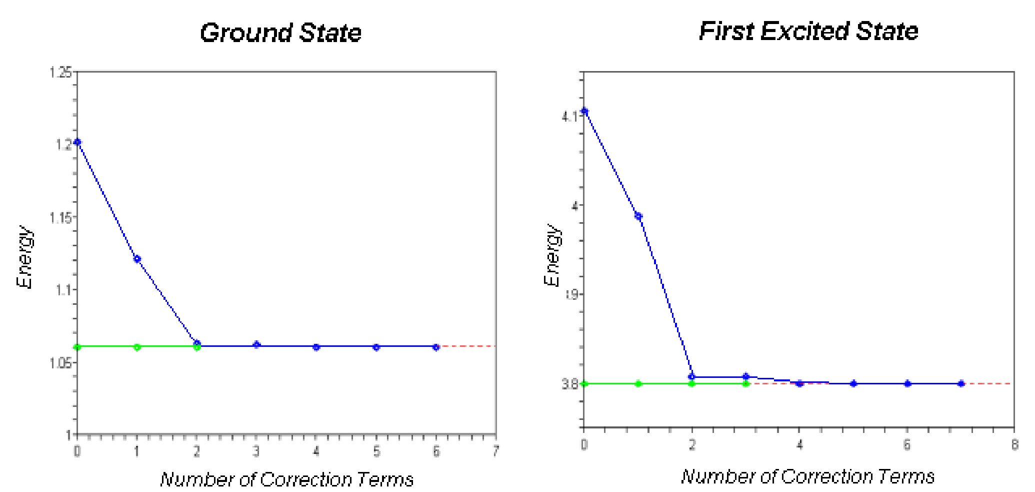

Figure 3

Figure 3. In the case of the x^4 potential, we show the systematic convergence for the ground and first excited state energies. Blue and green are the energies calculated from the first and second trial wave functions, respectively. Red line is the numerical solution.

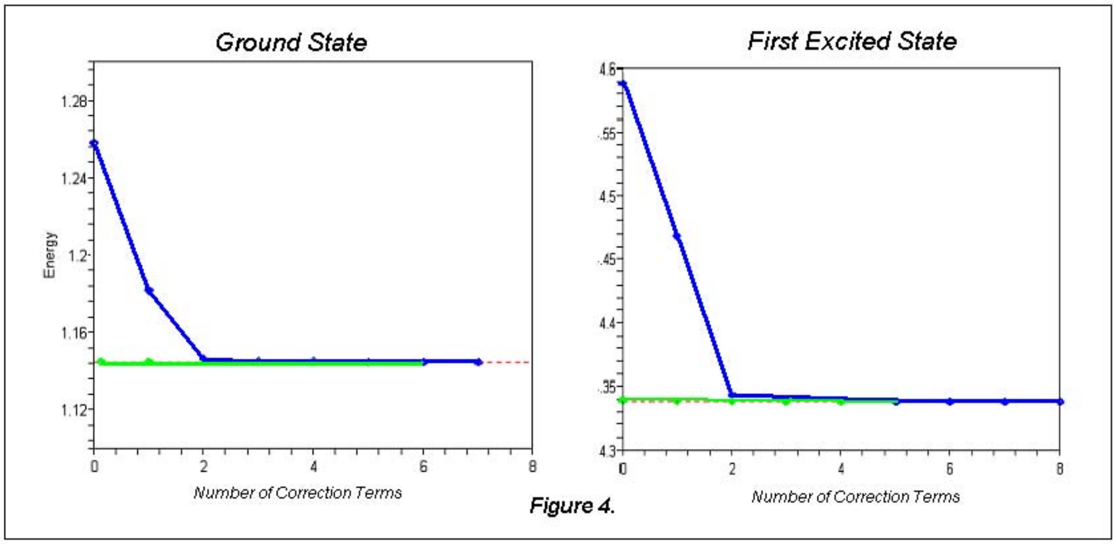

Figure 4.

Figure 4. In the case of the x^6 potential, we show the systematic convergence for the ground and first excited state energies. Blue and green are the energies calculated from the first and second trial wave functions, respectively. Red line is the numerical solution.

Another way to reveal the systematic improvement of the trial wave functions is to compare the effective potential V_{eff}, Eq. 4, and the real potential. As we can see in the following figures, Figure 5-6, these two potentials coincide with each other when the variational results approached almost precisely to that obtained from the numerical method.

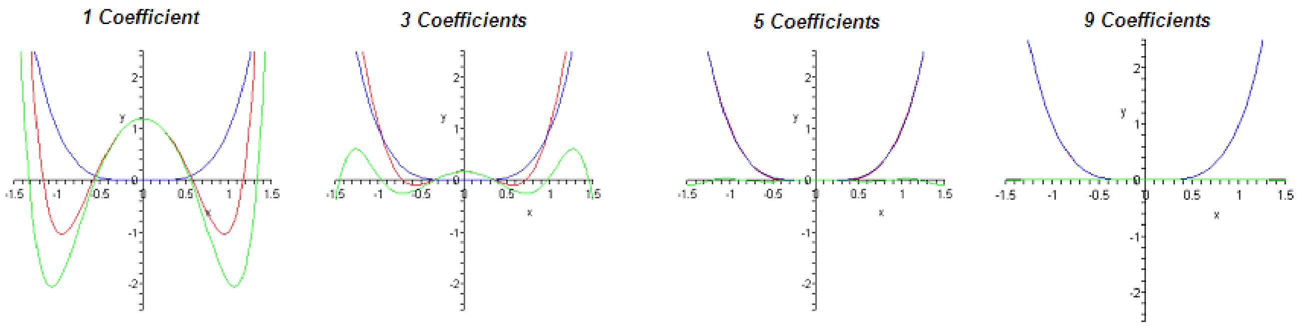

Figure 5.

Figure 5. In the case of the x^4 potential, we show how the effective potential evolves as we add more correction terms. The first plot is for one variational parameter and last one is when the number of parameters is increased to nine. The effective potential is in red, true potential is in blue, and green curve is their difference.

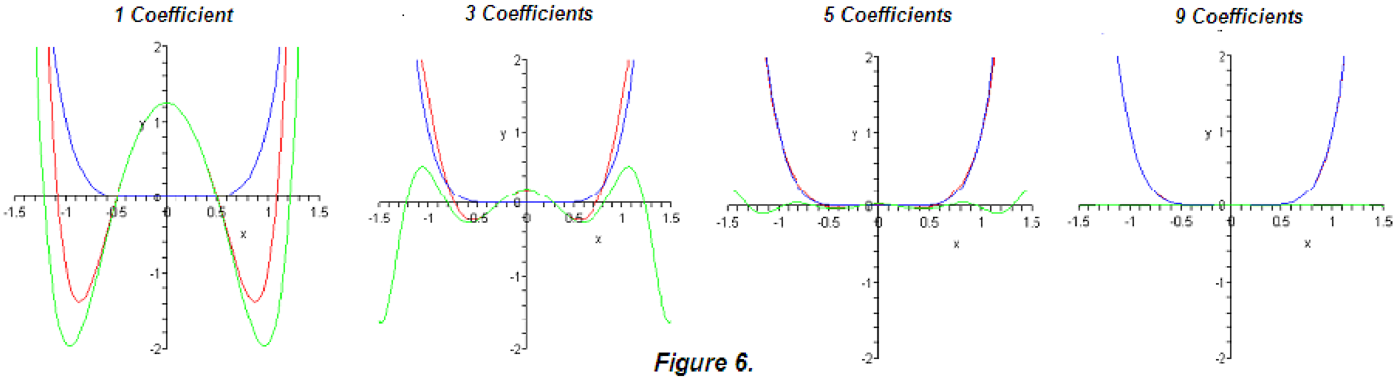

Figure 6.

Figure 6. In the case of the x^6 potential, we show how the effective potential evolves as we add more correction terms. The first plot is for one variational parameter and last one is when the number of parameters is increased to nine. The effective potential is in red, true potential is in blue, and green curve is their difference.

Finally, a remark is in order: when we were carrying out the numerical calculation, for convenience we set 2m, the Planck's constant $\hbar$, and coupling constants, α and β, of the potential in Eq. (1) equal to one. In fact, using a scale transformation we can derive a dimensionless differential equation: that is converting Eq. (1) to either

$$-\frac{d^2\psi}{dz^2}+z^4\psi=\varepsilon\psi \qquad (6),$$

by setting $z=\left(\frac{\hbar^2}{2m\alpha}\right)^{1/6}x$ and $\varepsilon=\left(\frac{2m}{\hbar^2}\right)^{2/3}\frac{E}{\alpha^{1/3}}$, or

$$-\frac{d^2\psi}{dz^2}+z^6\psi=\varepsilon\psi \qquad (7),$$

by setting $z=\left(\frac{\hbar^2}{2m\beta}\right)^{1/8}x$ and $\varepsilon=\left(\frac{2m}{\hbar^2}\right)^{3/4}\frac{E}{\beta^{1/4}}$.

IV. Conclusion

We showed that when using the variational method, systematic convergence to the numerical values is achieved by adding more variational parameters into the trial wave functions. We found that, among the two set of trial wave functions we introduced, the more sophisticated one provides more accurate eigenvalues. However, as we increase the number of parameters in both trial wave functions, they both reached practically the same values as that obtained from the Runge-Kutta numerical integration schemes, namely accurate to the sixth significant figures. When carrying out this project, we used the upgraded Maple 10 packages intensively and found that it is an effective and valuable tool in manipulating complex formulas and minimizing the parameters of our trial wave functions.

V. Acknowledgements

We would like to thank the Department of Physics at the University of Nebraska at Omaha (UNO) for the unique opportunity and inspiration it has offered us. This work started from taking the Quantum Mechanics II course from Dr. Wai-Ning Mei, his encouragement and guidance through out the entire project are deeply appreciated. We would also like to express our gratitude to Drs. Glen Sowell, Dan

Wilkins, and Robert Graham of the Physics Department, as well as Dr. Robert Smith of the Chemistry Department, for their guidance and support of the undergraduate body of the UNO physics department

VI. Appendix

In the process of applying the trial wave function II, we encountered the following integral:

$$\int_0^\infty \exp(-\mu x^4 - \nu x^2)dx \quad , \tag{A1}$$

where μ and ν are real and positive constants. This can be found in the standard mathematical handbook such as Table of Integrals, Series, and Products *(3 and 4)*. But the detailed derivation is not provided in many other mathematical tables, therefore we shall bridge the gap here in the Appendix.

To begin, we make use of two clever identities: first a relations hyper-trigonometric function,

$$\cosh(4\theta) = 8\sinh^4(\theta) + 8\sinh^2(\theta) + 1 \tag{A2}$$

Then we use the integral presentation of the modified Bessel function of fractional order σ, $K_\sigma(z)$ *(4):*

$$\int_0^\infty \exp[-z\cosh(\theta)]\cosh(\sigma\theta)d\theta \equiv K_\sigma(z) \tag{A3}$$

Now consider the substitution $x = \sqrt{\frac{\nu}{\mu}}\sinh(\theta)$, then the exponent of the integrand (A.1) becomes:

$$\mu x^4 + \nu x^2 = \frac{\nu^2}{\mu}\sinh^4(\theta) + \frac{\nu^2}{\mu}\sinh^2(\theta) \tag{A4}$$

Using **(A2)**, we have the following result:

$$\mu x^4 + \nu x^2 = \frac{\nu^2}{8\mu}\cosh(4\theta) - \frac{\nu^2}{8\mu} \tag{A5}$$

Then integral (A1) can be expressed as following

$$\int_0^\infty \exp(-\mu x^4 - \nu x^2)dx = \exp\left(\frac{\nu^2}{8\mu}\right)\int_0^\infty \exp\left[-\frac{\nu^2}{8\mu}\cosh(4\theta)\right]\sqrt{\frac{\nu}{\mu}}\cosh(\theta)d\theta \tag{A6}$$

Making use of identity (A3), then we get the known result in the handbook,

$$\int_0^\infty \exp(-\mu x^4 - \nu x^2)dx = \frac{1}{4}\sqrt{\frac{\nu}{\mu}}\exp\left(\frac{\nu^2}{8\mu}\right)K_{\frac{1}{4}}\left(\frac{\nu^2}{8\mu}\right) \tag{A7}$$

Furthermore, applyingA6 and the recurrence relation of Bessel functions,

$$\frac{d}{dz}K_{\sigma}(z) = K_{\sigma+1}(z) + \frac{\sigma}{z}K_{\sigma}(z) \qquad \text{(A8)}$$

we can evaluate much more complicated integrals like:

$$\int_0^{\infty} x^{2n}\exp\left(-\mu x^4 - \nu x^2\right)dx \qquad \text{(A9)}$$

where n is an integer. For example:

$$\int_0^{\infty} x^2\exp(-\mu x^4 - \nu x^2)dx = -\frac{\partial}{\partial\nu}\int_0^{\infty}\exp(-\mu x^4 - \nu x^2)dx$$

$$= \left[\frac{1}{16}\sqrt{\frac{\nu^3}{\mu^3}}K_{\frac{5}{4}}\left(\frac{\nu^2}{8\mu}\right) - \left(\frac{1}{4}\sqrt{\frac{1}{\mu\nu}} + \frac{1}{16}\sqrt{\frac{\nu^3}{\mu^3}}\right)K_{\frac{1}{4}}\left(\frac{\nu^2}{8\mu}\right)\right]\exp\left(\frac{\nu^2}{8\mu}\right) \qquad \text{(A10)}$$

and also:

$$\int_0^{\infty} x^4\exp(-\mu x^4 - \nu x^2)dx = -\frac{\partial}{\partial\mu}\int_0^{\infty}\exp(-\mu x^4 - \nu x^2)dx$$

$$= \left[-\frac{1}{32}\sqrt{\frac{\nu^5}{\mu^5}}K_{\frac{5}{4}}\left(\frac{\nu^2}{8\mu}\right) + \left(\frac{3}{16}\sqrt{\frac{\nu}{\mu^3}} + \frac{1}{32}\sqrt{\frac{\nu^5}{\mu^5}}\right)K_{\frac{1}{4}}\left(\frac{\nu^2}{8\mu}\right)\right]\exp\left(\frac{\nu^2}{8\mu}\right) \qquad \text{(A11)}$$

The rest, when n > 2, can be performed in a similar manner.

Our Maple work sheets are available for the interested readers, please send request to the attached e-mail addresses.

VII. References

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