Anharmonic Oscillator Potentials:

Exact and Perturbation Results

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Abstract

In order to determine the first four energy levels of our anharmonic potential, we will compute the first four eigenvalues of the anharmonic oscillator potential with a quartic term using Heun polynomials and Maple software packages. We will then compare them to the results obtained from the conventional perturbation method, treating the quartic term as perturbation up to the third order. Through this it can be shown that generally the two methods agree well with each other when the perturbing potential is weak. Nevertheless, the perturbation results will start to deviate from those of the exact solutions at stronger perturbation potentials and higher excited states.

I. Introduction

When learning the time-independent perturbation method of quantum mechanics, most students are taught that as long as the perturbation potential is not strong, the corrections in eigenvalues and eigenfunctions can be calculated systematically order by order. The statement is intuitively reasonable, yet not complete. We learned from the seminal paper of Bender and Wu [1] that it was proved that the perturbation series for the ground state energy of the anharmonic oscillator with only the quartic term diverges for any non-zero coupling constant. A simple way to explain it is in the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\omega^2 x^2 + \alpha x^4 \right]\psi = E\psi . \qquad (1)$$

That is, even though α, the coupling constant of the quartic term, can be very small, after large enough values of x the quartic potential αx^4 eventually supersedes the harmonic potential $m\omega^2/2$, and it can no longer be considered weak. Therefore during practical computation, for the perturbation scheme to be applicable not only do we have to be certain that the coupling constant is small enough, but we also have to examine the region of validity. However, when the method is taught in most commonly adopted textbooks, major efforts are spent on deriving the general formulas of energy and wave function corrections and applying them to a few well known examples as mentioned above, but no demonstrations are provided. In all likelihood, the inability to solve Eq. (1) analytically is one of the reasons. By now, we have learned that Schrödinger equations like Eq. (1) can be solved in terms of Heun polynomials that are explained thoroughly in the references [2] mentioned in Maple Help pages. Computer algebra software packages in Maple 14 are capable of evaluating these special functions, rendering the exact solution attainable.

In this work, we will calculate the total energies of the first four eigenvalues of the anharmonic oscillator with only the quartic term, using both the perturbation and numerical methods. First we shall summarize the procedures in deriving the leading three orders of energy

corrections and apply them to the quartic potential, and then we will highlight the numerical schemes in computing the ground and first three excited state energies of the anharmonic oscillator potentials. Finally we will compare results obtained from these two methods and discuss the applicability of the perturbation method.

II. Theory

Before starting the perturbation and numerical calculations, we reduce the Schrödinger equation, Eq. (1), into a dimensionless differential equation: first we substitute $x = \beta z$, where β is an undetermined parameter, and divide the whole Eq. (1) by $\dfrac{\hbar^2}{2m\beta^2}$. We notice, then, that as we

set $\beta = \sqrt{\dfrac{\hbar}{m\omega}}$, $\gamma = \dfrac{2\alpha\hbar}{m^2\omega^3}$ and $\varepsilon = \dfrac{2E}{\hbar\omega}$, a new differential equation emerges,

$$\left[-\frac{d^2}{dz^2} + z^2 + \gamma z^4 \right]\psi = \varepsilon\psi . \tag{2}$$

From there on, it is clear that only the parameter γ in this problem controls the strength of the perturbation potential.

It is well known that besides the simple harmonic oscillator and hydrogen atom, most of the time-independent Schrödinger equations cannot be solved analytically. For many practical cases, we solve the problems by applying the perturbation method mentioned in Griffiths' quantum mechanics textbook [3]. That is, we split the Hamiltonian $\hat{H}$ into two parts: one is the unperturbed Hamiltonian H^0, for which we know all the associated eigenvalues $E_n^{(0)}$ and eigenstates $\psi_n^{(0)}$, and the additional term H', usually referred to as perturbation,

$$\hat{H} = H^0 + \lambda H'. \tag{3}$$

Here λ is a coupling constant which is commonly used to keep track the strength of perturbation H' and is ideally a small number. Later, however, it was turned to 1, so it only serves as an

indicator while deriving the energy corrections. Then we assume the eigenvalues E_n and eigenstates ψ_n of $\hat{H}$ can be expressed as power series in λ:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ...$$

$$\text{and} \quad \psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \lambda^3 \psi_n^{(3)} + ... \tag{4}$$

where $E_n^{(1)}$, $E_n^{(2)}$ and $E_n^{(3)}$ are the first, second and third order correction to the eigenvalues respectively, and $\psi_n^{(1)}$, $\psi_n^{(2)}$ and $\psi_n^{(3)}$ are the first, second and third order correction to the eigenfunctions, respectively. After we substitute Eq. (2) into the Schrödinger equation, sort out terms in the order of λ and make use of the orthogonality and completeness properties of the eigenfunctions of $\hat{H}$, the lower order corrections of eigenvalues and eigenfunctions are derived as in standard quantum mechanics textbooks [3]. In simple notation, we only present the energy corrections: first let

$$V_{mn} = \left\langle \psi_m^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle \quad \text{and} \quad \Delta_{mn} = E_m^{(0)} - E_n^{(0)}, \tag{5} \quad \text{then we have}$$

$$E_n^{(1)} = V_{nn}, \qquad E_n^{(2)} = \sum_{m \neq n} \frac{|V_{nm}|^2}{\Delta_{nm}}, \qquad \text{and} \qquad E_n^{(3)} = \sum_{l,m \neq n} \frac{V_{nl} V_{lm} V_{ml}}{\Delta_{nl} \Delta_{nm}} - V_{nn} \sum_{m \neq n} \frac{|V_{nm}|^2}{\Delta_{nm}^2}. \tag{6}$$

In this work we only go up to the third order correction; of course, it is possible to pursue higher orders by following the procedures cited in the quantum mechanics textbook [3]. Generally in the summations of Eq. (4) we should include all the non-zero matrix elements. Fortunately the simple harmonic oscillator is our unperturbed Hamiltonian H^0, and the perturbation potential we considered is quartic, so there are only a few non-vanishing terms due to the raising and lowering ladder operators constructed from the original eigenstates. This is presented in Chapter 2 of the quantum mechanics textbook [4], and energy corrections can be computed accordingly.

  In fact, the analytical solutions of the Schrödinger equation, Eq. (2), can be expressed in terms of the linear combination of two linearly independent Heun Triconfluent equations HeunT$_1$ and HeunT$_2$ [2], abbreviated as H$_1$ and H$_2$. Both of these are complex functions of the scaled

variable z, parameter γ, and eigenvalue ε. They have different asymptotic behaviors. One may reach zero when $z \to \infty$ and diverge as $z \to -\infty$, and the other one is exactly the opposite:

$$\psi(z,\gamma,\varepsilon) = C_1 H_1(z,\gamma,\varepsilon) + C_2 H_2(z,\gamma,\varepsilon) \tag{7}$$

where C_1 and C_2 are two arbitrary constants to be determined from the asymptotic conditions. Since we are looking for bound state solutions—that is, the wave functions have to vanish as z approaches to both positive and negative infinities—

$$\psi(z,\gamma,\varepsilon) \to 0 \text{ when } z \to \pm\infty. \tag{8}$$

To facilitate numerical calculations, we require that the wave functions vanish at a finite range $\pm R$ to approximate the asymptotic behavior of wave functions at positive and negative infinity. Actually, we observe that the first few excited state wave functions of simple harmonic oscillators approach zero around R= 4 to 5. Thus we first assume R=4.5, with given γ, and we numerically compute ε by solving the following 2x2 determinant equation which is only a function of ε,

$$\begin{vmatrix} H_1(R,\gamma,\varepsilon) & H_2(R,\gamma,\varepsilon) \\ H_1(-R,\gamma,\varepsilon) & H_2(-R,\gamma,\varepsilon) \end{vmatrix} = 0 \tag{9}$$

It turns out both the HeunT_1 and HeunT_2 are complex and often huge, hence they require quite a lot of digits—roughly 30 to 70 depending on different asymptotic conditions—and computation time to reach convergence. Yet when reaching the zeroes of the determinant, Eq. (7) is purely real and we find that the roots correspond to the eigenvalues of Eq. (2). In this work, we only compute the first four eigenvalues and use them to plot the wave functions. Results with various γ, such as energies obtained from both the numerical and perturbation methods and wave functions computed from Heun polynomials, can be seen in the Section III. Finally, we select R carefully: first we set R= 4.5, then gradually increase it to 6 and notice the values of the roots change minutely. We declare that R ~ 5 is effectively equivalent to infinity. Afterward, we plot the wave functions and observe that indeed all the wave functions vanish before R = 5.

III. Results and discussion

Based on Equations (5) and (6), we calculate the first four perturbed total energies of the anharmonic oscillator, ε_0 to ε_3, up to the third order γ^3,

$$\varepsilon_0 = 1 + \frac{3}{4}\gamma - \frac{21}{16}\gamma^2 + \frac{333}{64}\gamma^3$$

$$\varepsilon_1 = 3 + \frac{15}{4}\gamma - \frac{165}{16}\gamma^2 + \frac{3915}{64}\gamma^3$$

$$\varepsilon_2 = 5 + \frac{39}{4}\gamma - \frac{615}{16}\gamma^2 + \frac{20079}{64}\gamma^3$$

$$\varepsilon_3 = 7 + \frac{75}{4}\gamma - \frac{1575}{16}\gamma^2 + \frac{66825}{64}\gamma^3 \tag{10}$$

Just by inspecting the increasing coefficients, we realize that in order to have reasonable perturbed energies, the values of γ have to be very small.

In Table 1 and Figure 1, we present the comparison of results obtained from numerical and perturbation methods.

	γ	Numerical	2nd Order Perturbation	Percent Difference (2nd Order)	3rd Order Perturbation	Percent Difference (3rd Order)
n = 0	0.05	1.03473	1.03422	0.0494%	1.03487	-0.0134%
	0.075	1.05043	1.04887	0.1488%	1.05106	-0.0602%
	0.1	1.06529	1.06188	0.3206%	1.06708	-0.1679%
n = 1	0.05	3.16723	3.16172	0.1740%	3.16937	-0.0674%
	0.075	3.23967	3.22324	0.5071%	3.24905	-0.2895%
	0.1	3.30687	3.27186	1.0583%	3.33305	-0.7916%
n = 2	0.05	5.41726	5.39141	0.4772%	5.39141	0.4772%
	0.075	5.59031	5.51504	1.3464%	5.51504	1.3465%
	0.1	5.74796	5.59063	2.7371%	5.59063	2.7372%
n = 3	0.05	7.77027	7.69141	1.0149%	7.82192	-0.6648%
	0.075	8.07718	7.85254	2.7812%	8.29304	-2.6724%
	0.1	8.35268	7.89063	5.5318%	8.93477	-6.9688%

Table 1. Comparison of the first four eigeneneriges calculated from numerical and perturbation methods, both second and third order.

We further notice two general features in perturbation results up to second order: first, the agreements are far better at the low-lying states than those of the higher excited states. The percentage discrepancies in n=0 and 1 are less than 1%, and those of n=2 and 3 are greater than 1%. Second, when γ=0.05, the percentage discrepancies for all the first four states are small and not greater than 1% except n=3. As γ increases to 0.075 and 0.1, most of the percentage discrepancies exceed 1%; particularly, the third excited state (n=3) reaches 5.5%.
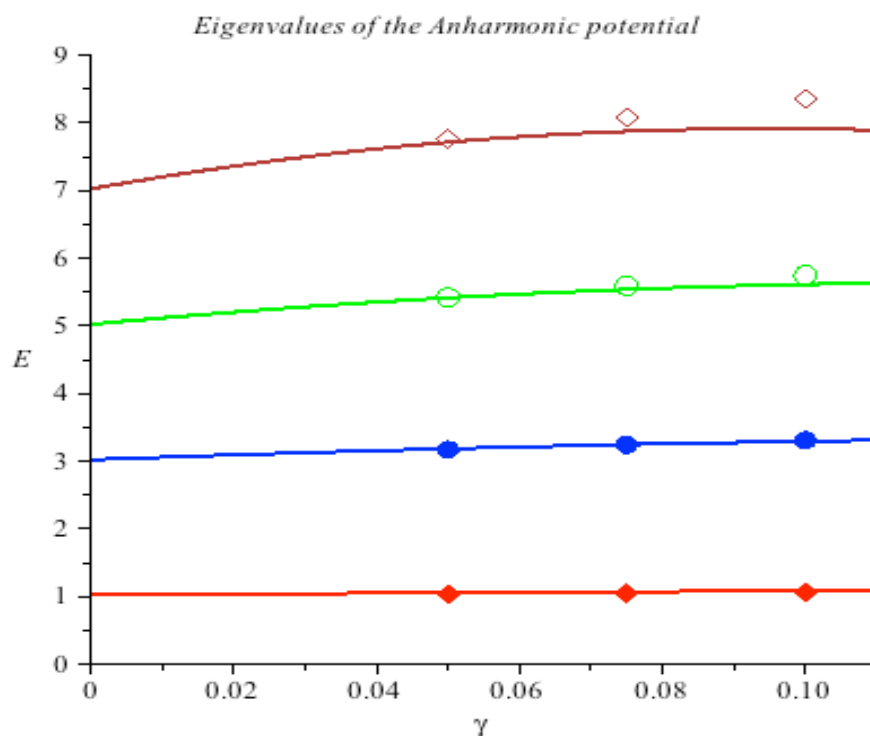
Figure 1. Comparison of the first four eigeneneriges calculated from numerical (discrete symbols) and second order perturbation methods (continuous curves). Ground state (red), first (blue), second (green) and third (brown) excited states.

We can interpret these features from observing the wave functions displayed in Figure 2: notice that the wave functions of the ground state (red) and first excited state (blue) vanish as z~3, whereas those of the second (green) and third (brown) excited states drop to zero when z at least exceeds z~3.5. This is a crucial change, since we can easily deduce that the quartic potential z^4 surpasses harmonic potential z^2 at the crossover range z_c~3.16, where $z_c=1/\sqrt{\gamma}$, when γ=0.1.

This implies the basis that the perturbation method is valid when the perturbation is relatively weak or less than 10%. To further clarify our claim, we carry out the same analysis by including the third order correction: similarly in Table 1, we find that the improvements on the low-lying states, n=0 and 1, are small and incremental, yet overshoot the exact values. The third order results are larger than the exact values, whereas those of the second order are less.
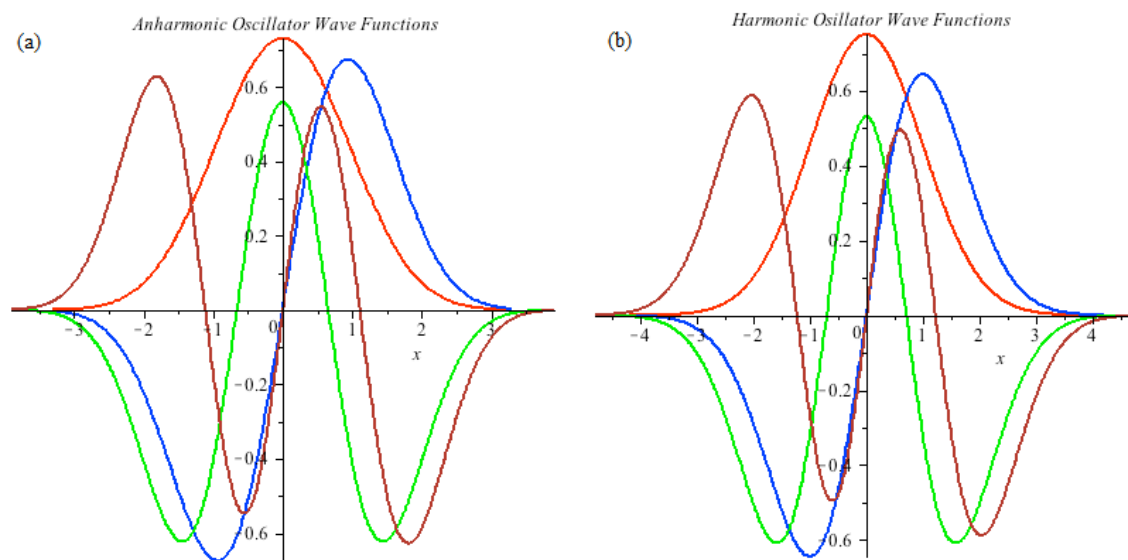

Figure 2. (a) Wave functions of the first four eigenstates of the anharmonic potential with γ = 0.1: ground state (red), first (blue), second (green) and third (brown) excited states. (b) First four eigenstate wave functions of the harmonic oscillator are used for comparison. Apparently wave functions in (a) and (b) are similar, but notice that the ranges of (b) are longer.

This effect is more prominent for higher excited states like n=2 and 3: the percentage discrepancies change from 2.74 and 5.5% in second order correction results to -2.72 and -7.0% for n=2 and 3 respectively, in third order correction results, as shown in Table 1 and Figure 3.
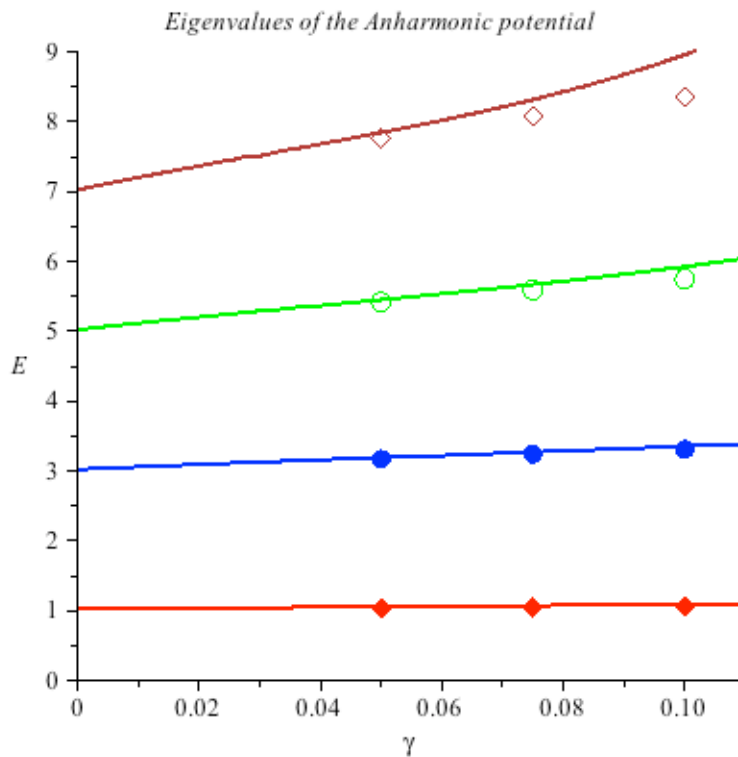
Figure 3. Comparison of the first four eigeneneriges calculated from numerical (discrete symbols) and third order perturbation methods (continuous curves). Ground state (red), first (blue), second (green) and third (brown) excited states.

In other words, adding more correction terms may lead to oscillatory behavior in total perturbed energies. Nevertheless, in order to verify this assertion it is necessary to have higher-order calculations, which as mentioned in the quantum mechanics textbook [3], is a lengthy calculation. Hopefully this calculation will be carried out in the future.

Finally, like the previous works [5, 6] published at the Journal of Undergraduate Research in Physics by physics majors from the University of Nebraska at Omaha, we have intensively used Maple packages to perform all the analytical and numerical calculations. We find the packages are efficient and helpful in our work. Our worksheets are available for interested readers. Please send requests to the attached addresses.

IV. Conclusion

In summary, we calculated the first four eigenenergies of the harmonic oscillator potential with the quartic term using numerical and conventional perturbation methods. We found that the two methods agree well with each other when the perturbing potential is weak and particularly at the low-lying states. As the perturbing potential gets stronger, particularly at the higher excited states, we noticed the perturbation results start to deviate from those obtained from the numerical schemes. We elucidated this behavior by comparing the strengths of harmonic and quartic potentials and uncovered that the conventional perturbation method starts to be ineffective when the wave functions exceed the crossover range.

V. Acknowledgements

VI. References

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