

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:

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

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{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} :

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

where ψ_{trial} is a trial wave function, when we happen to choose the true wave function (J). 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{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.

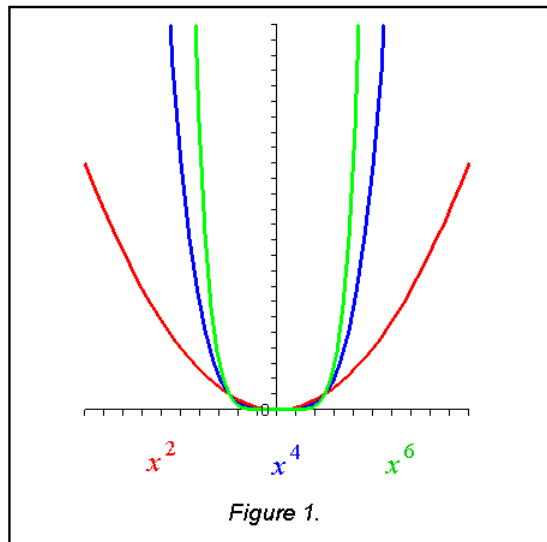
$$E_{\text{tot}} = \langle \text{KE} \rangle + \langle \text{PE} \rangle \quad (3)$$

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:

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

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

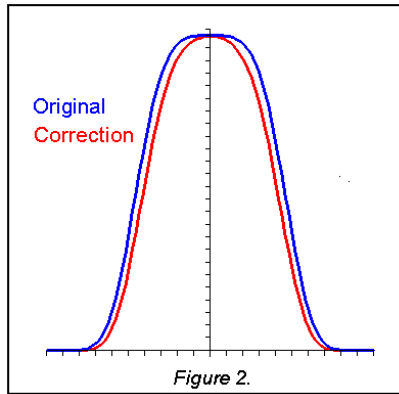
In this project we applied the variational principle to two anharmonic potentials: x^4 and x^6 , similar study has been carried out before (2), in which different set of trial wave functions were used to calculate the ground state and first excited state energies. Some of the values so obtained were 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,



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.



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:

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

where a, b, c, \dots, 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 than 0.1%, but utilizing the second trial wave function requires *a priori* 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 of 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

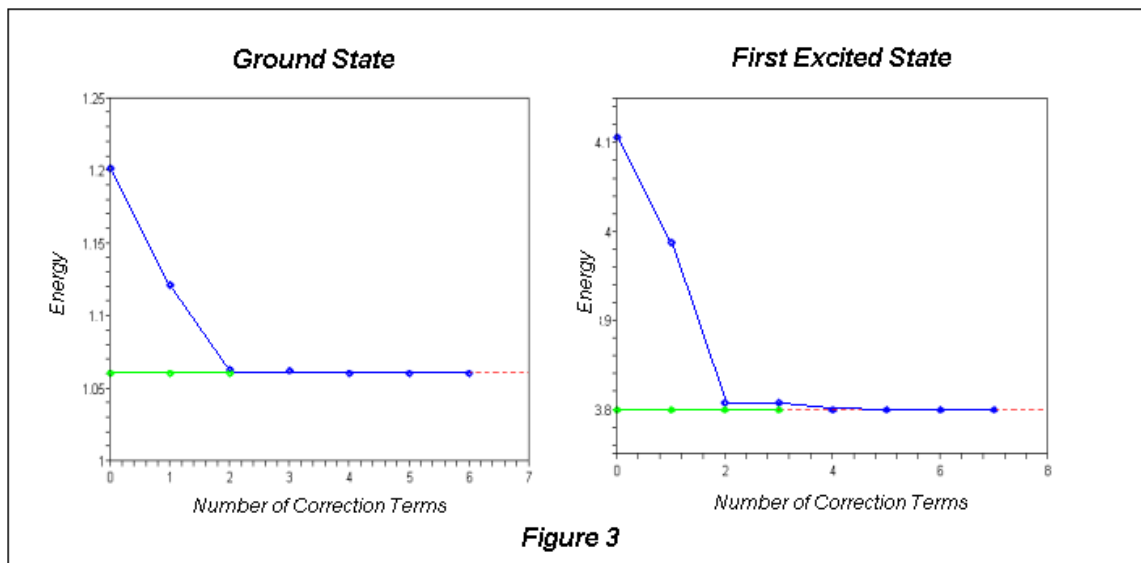


Figure 3. In the case of the x^4 potential, we show the systematic convergence for the ground and first excited state energies. Blue and green are the energies calculated from the first and second trial wave functions, respectively. Red line is the numerical solution.

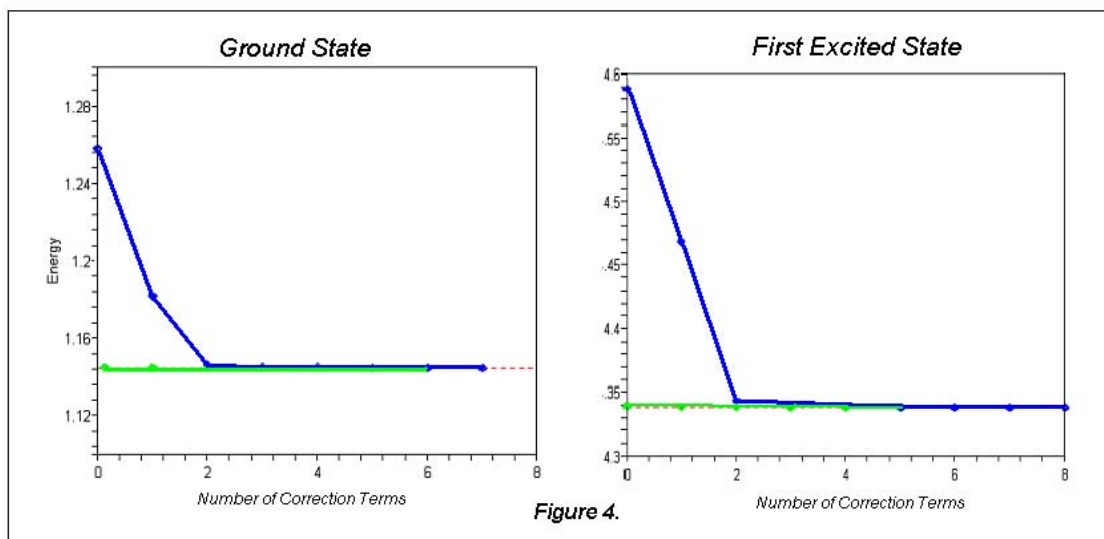


Figure 4. In the case of the x^6 potential, we show the systematic convergence for the ground and first excited state energies. Blue and green are the energies calculated from the first and second trial wave functions, respectively. Red line is the numerical solution.

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.

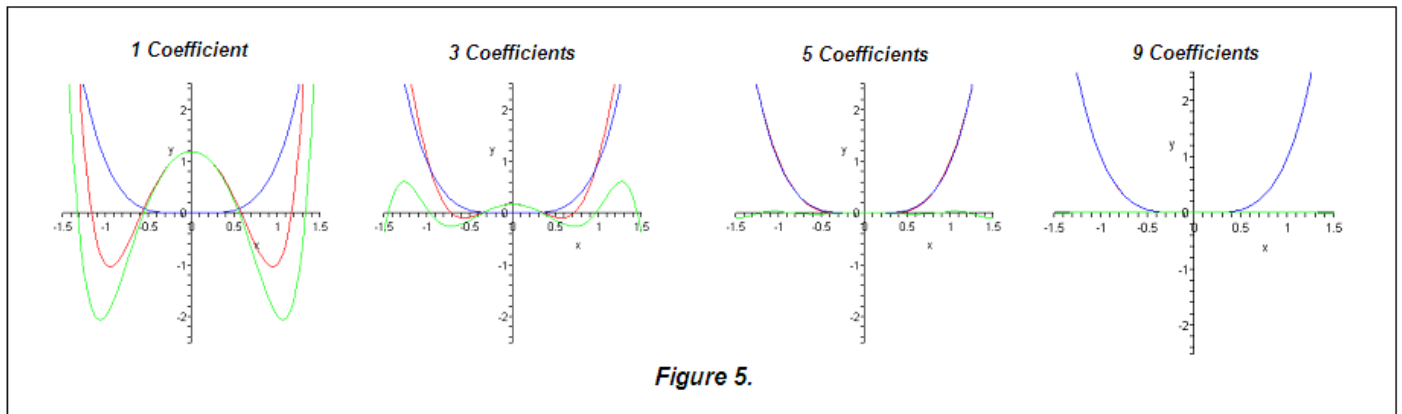


Figure 5.

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.

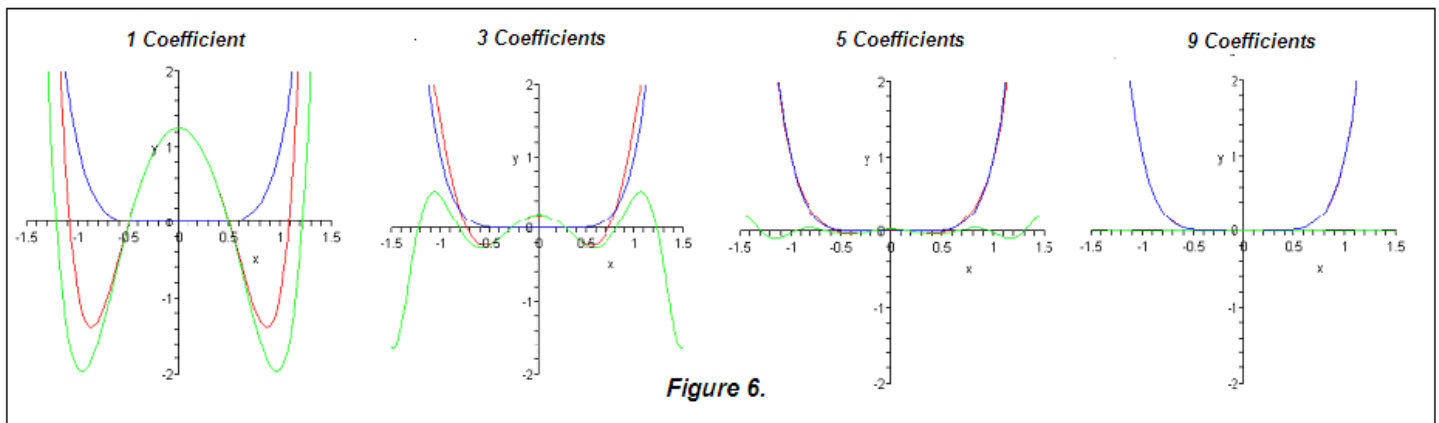


Figure 6.

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

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

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

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

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

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VI. Appendix

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

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

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,

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

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

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

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

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

Using (A2), we have the following result:

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

Then integral (A1) can be expressed as following

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

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

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

Furthermore, applying A6 and the recurrence relation of Bessel functions,

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

we can evaluate much more complicated integrals like:

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

where n is an integer. For example:

$$\begin{aligned} \int_0^{\infty} x^2 \exp(-\mu x^4 - \nu x^2) dx &= -\frac{\partial}{\partial \nu} \int_0^{\infty} \exp(-\mu x^4 - \nu x^2) dx \\ &= \left[\frac{1}{16} \sqrt{\frac{\nu^3}{\mu^3}} K_{\frac{5}{4}}\left(\frac{\nu^2}{8\mu}\right) - \left(\frac{1}{4} \sqrt{\frac{1}{\mu\nu}} + \frac{1}{16} \sqrt{\frac{\nu^3}{\mu^3}} \right) K_{\frac{1}{4}}\left(\frac{\nu^2}{8\mu}\right) \right] \exp\left(\frac{\nu^2}{8\mu}\right) \end{aligned} \quad (\text{A10})$$

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

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

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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