

COMPUTATIONAL PHYSICS & ASTRONOMY (188B)

# Project III: Eigenvalue Problems in Quantum Mechanics

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## 1 Quantum Oscillators

### 1.1 Introduction

Quantum mechanics involves finding a solution to Schroedinger's Equation, a second order partial-differential equation (PDE), for a given energy potential  $V(\mathbf{r})$ . The one-dimensional, time-independent formulation of Schroedinger's Equation is given by,

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

where  $E$  represents the energy of the system. In the above PDE,  $\psi(x)$  represents the solution for the given energy potential and is known as a *wavefunction*.

All wavefunctions and quantum states lie within the Hilbert space, a vector space that generalizes the notion of Euclidean space [?]. Though the Hilbert space has several properties, one of the most consequential is that it is a vector space on which the following inner product is defined,

$$\langle \psi_m(x) | \psi_n(x) \rangle = \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx \quad (2)$$

where  $\psi_m^*(x)$  is the complex conjugate of  $\psi_m(x)$ . Wavefunctions are said to be *orthonormal*, meaning

$$\begin{aligned} \langle \psi_m | \psi_n \rangle &= 1 && \text{for } n = m, \\ \langle \psi_m | \psi_n \rangle &= 0 && \text{for } n \neq m \end{aligned} \quad (3)$$

Additionally, the Hilbert space is not only a vector space but an *inner product* space. This means that the inner product as defined in equation (2) is linear, the inner product of element with itself is positive and definite (as shown in equation (3)), and the inner product of a pair of elements is equal to the inner product of the complex conjugate of the swapped elements, or  $\langle \psi_n | \psi_m \rangle = \langle \psi_m | \psi_n \rangle^*$ .

Something that has been overlooked is the meaning the wavefunction  $\psi(x)$ , and how to find physical observables. The wavefunction  $\psi(x)$  has no actual meaning on its own and it does not necessarily represent the trajectory of a particle as in the classical case. Rather,  $\psi(x)$  only has meaning when multiplied by its complex conjugate, which is given by  $\rho(x) = |\psi(x)|^2 = \psi^*(x)\psi(x)$ .  $\rho(x)$  is known as the *probability density* for a quantum state  $\psi(x)$ . A probability density is a statistical value, and physical observables can be found by taking the *expectation value*. For a physical observable  $A$ , the expectation value is the integral of  $A\rho(x)$  over all space, or

$$\langle A \rangle = \int_{-\infty}^{\infty} A\rho(x) dx \quad (4)$$

Equation (4) can be reformulated in terms of the bra-ket notation used to express the inner product in (2). In bra-ket notation, the expectation value of  $A$  is given by,

$$\langle \psi_m | A | \psi_n \rangle = \langle A \rangle = \int_{-\infty}^{\infty} A\rho(x) dx \quad (5)$$

In linear algebra, a linear operator is a transformation that maps one vector space to another vector space. If a linear operator  $\hat{A}$  maps a vector space onto itself, then we have the expression,

$$\hat{A}\psi(x) = \lambda\psi(x) \quad (6)$$

We can find the expectation value of an operator  $\hat{A}$  using equations (6) and (5), and the fact that the inner product is linear, giving

$$\langle\psi_m|\hat{A}|\psi_n\rangle = \langle\psi_m|\lambda_n\psi_n\rangle = \lambda_n\langle\psi_m|\psi_n\rangle \quad (7)$$

In quantum mechanics, values for physical observables such as energy, position, and momentum are found by using the operators  $\hat{H}$ ,  $\hat{x}$ , and  $\hat{p}$ , respectively, on the quantum state or wave function  $\psi(x)$ . The linear operator for position and momentum is given by  $\hat{x} = x$  and  $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ , respectively. The linear operator for energy,  $\hat{H}$ , is called the Hamiltonian and is analogous to the Hamiltonian of classical mechanics in that it is the sum of the kinetic energy and potential energy of particle, expressed in terms of the momentum and position operators. In other words, the Hamiltonian operator is given by,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \quad (8)$$

Notice that equation (8) is contained within Schroedinger's Equation. We can then rewrite equation (1) in terms of the Hamiltonian operator,

$$\hat{H}\psi(x) = E\psi(x) \quad (9)$$

The Hamiltonian operator, therefore, is a linear operator that maps the Hilbert space onto itself, since the result is the original wavefunction  $\psi(x)$  times a constant  $E$ . That constant is the energy of the state  $\psi(x)$ . If the wavefunctions of a quantum state are known, we can find the energy of the state by finding the expectation value of the Hamiltonian operator. We find the expectation value for an operator using equation (7), and for  $\hat{H}$  this gives

$$\langle\psi_m|\hat{H}|\psi_n\rangle = E_n\langle\psi_m|\psi_n\rangle \quad (10)$$

For the remainder of the report, we will be interested in finding the wavefunctions and their energy expectation values for an anharmonic oscillator potential and a double well potential, using the wavefunctions for a harmonic oscillator potential as a basis. Of particular importance in accomplishing this are equations (9) and (10), which are equivalent to eigenvalue/eigenvector problem of linear algebra. The explicit methods used and they relate to the above discussion are covered in the next section.

## 2 Methods

In quantum mechanics, energy is *quantized* meaning it is determined by a discrete integer  $n = 0, 1, 2, \dots$ , known as the quantum number, and is not continuous. Because of this, Schroedinger's Equation of the form in (9) becomes

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \quad (11)$$

where  $\psi_n$  is a discrete wavefunction with associated discrete energy  $E_n$  and quantum number  $n$ . Recall that we can find the expectation value of the Hamiltonian operator using equation (10), which is already discretized. Using the fact that wavefunctions are orthonormal, as shown in equation (3), we can rewrite equation (10) using the Kronecker-Delta function  $\delta_{nm}$ , which is zero for  $m \neq n$  and one for  $m = n$ . We also implement the notation  $H_{mn} = \langle u_m|\hat{H}|u_n\rangle$ , giving the following expression for the expectation value of the Hamiltonian for a given quantum number  $n$ ,

$$H_{mn} = E_n\delta_{mn} \quad (12)$$

If we find the energy expectation values over all  $n$ , we can construct an  $n \times n$  matrix  $\overleftrightarrow{H}$ , known as the Hamiltonian matrix. Because all operators in quantum mechanics are Hermitian, the matrix  $\overleftrightarrow{H}$  is also Hermitian, meaning it is symmetric, its eigenvalues are real-valued, and its eigenvectors are orthonormal. Because the energy of a quantum state must be real-valued and because we know wavefunctions are orthonormal, we can rewrite equation (11) in matrix form,

$$\overleftrightarrow{H} \overrightarrow{\psi}_n = E_n \overrightarrow{\psi}_n \quad (13)$$

Therefore, the problem of finding the wavefunctions and their associated energies for a given Hamiltonian has been reduced to the *eigenvalue problem* of linear algebra.  $\overrightarrow{\psi}_n$  is an eigenvector, or an *eigenfunction*, with eigenvalue  $E_n$  and written in terms of some basis functions  $\overrightarrow{u}_m$  for  $m = 0, 1, 2, \dots$ . The eigenvalues are found using

$$\det(\overleftrightarrow{H} - E_n \overleftrightarrow{I}) = 0 \quad (14)$$

where  $\det$  indicates the determinant and  $\overleftrightarrow{I}$  is the identity matrix. The eigenvectors are then found by solving (13) for a given eigenvalue.

For this assignment, we used the Python function `eigh()` from the SciPy library to find both the eigenvalues and eigenfunctions of a given Hamiltonian matrix. The function `eigh()` requires that the input matrix be Hermitian. This is because Hermitian matrices can be reduced to a real symmetric tridiagonal matrix using  $N - 2$  similarity transforms, given by

$$\overleftrightarrow{A} = \overleftrightarrow{T} \overleftrightarrow{A} \overleftrightarrow{T}^{-1} \quad (15)$$

for an  $N \times N$  Hermitian matrix  $\overleftrightarrow{A}$ . Because all of our Hamiltonian matrices are assumed to be Hermitian in quantum mechanics, we are able to use the function `eigh()` without worry. Once the Hamiltonian matrix is transformed into a tridiagonal matrix, a QR algorithm is applied. A QR algorithm decomposes the Hermitian Hamiltonian matrix into an orthogonal matrix and an upper triangular matrix and multiplies the factors in reverse order, eventually finding the eigenvalues and eigenvectors after continually repeating this process [?]. Using this method we can avoid the “high order polynomial problem” resulting from finding the determinant of equation (14) when the basis of  $N$  equations is large. Much work has gone into developing algorithms to solve eigenvalue problems and the method above only scales quadratically for a basis of  $N$  equations.

We now discuss the three quantum mechanical problems considered in this assignment, in particular the origin of their Hamiltonian matrices.

## 2.1 Harmonic Oscillator

Recall that the potential energy for a harmonic oscillator is given by  $V(x) = \frac{1}{2}x^2$ . In terms of the position operator  $\hat{x}$ , the potential energy is then  $V(x) = \frac{1}{2}\hat{x}^2$ . Using equation (8), the Hamiltonian operator for the harmonic oscillator is therefore

$$\hat{H}_0 = \frac{1}{2}(\hat{p}^2 + \hat{x}^2) \quad (16)$$

where our units for energy, momentum, and distance are now in  $hf$ ,  $(mhf)^{1/2}$ , and  $(4\pi^2 fm/h)^{-1/2}$ , respectively, where  $h$  is Planck’s constant,  $f$  is the natural frequency of the oscillator, and  $m$  is the mass of the particle. These units will be used throughout the report.

The one-dimensional, time-independent Schrödinger Equation can be solved analytically for the harmonic oscillator Hamiltonian operator. The discrete energy eigenvalues are given by

$$E_n = n + \frac{1}{2} \quad \text{for } n = 0, 1, 2, \dots \quad (17)$$

And the eigenfunctions  $u_n(x)$  are given by

$$u_n(x) = (2^n n! \sqrt{\pi})^{-1/2} \exp(-x^2/2) \mathcal{H}_n(x) \quad \text{for } n = 0, 1, 2, \dots \quad (18)$$

$\mathcal{H}_n(x)$  is a Hermite polynomial defined recursively by

$$\mathcal{H}_{n+1}(x) = 2x\mathcal{H}_n(x) - 2n\mathcal{H}_{n-1}(x) \quad (19)$$

In this report we used the initial polynomials  $\mathcal{H}_0(x) = 1$  and  $\mathcal{H}_1(x) = 2x$  to find all subsequent Hermite polynomials. The eigenfunctions defined by equation (18) will be used as the basis functions for all Hamiltonian matrices and all eigenfunctions throughout this report, including the harmonic oscillator Hamiltonian matrix. The eigenfunctions  $u_n(x)$  are both the basis functions and the eigenfunctions of the Harmonic oscillator matrix  $\hat{H}_0$ , meaning the matrix will be diagonal. Indeed, with the energy expectation values given by (17), we immediately see that the harmonic oscillator Hamiltonian matrix elements are given by

$$[H_0]_{nm} = (n + \frac{1}{2})\delta_{nm} \quad (20)$$

a diagonal matrix.

## 2.2 Anharmonic Oscillator

The anharmonic oscillator potential contains the same terms as the potential energy of the harmonic oscillator but with a second-order, anharmonic correction added for more realistic modeling of physical systems. The anharmonic potential energy in terms of the position operator is given by  $V(x) = \frac{1}{2}x^2 + \lambda x^4$ , where  $\lambda$  sets the strength of the anharmonic term. Our Hamiltonian operator for the anharmonic oscillator is then given by

$$\hat{H} = \hat{H}_0 + \lambda \hat{x}^4 \quad (21)$$

where  $\hat{H}_0$  is the Hamiltonian operator for the harmonic oscillator. Schroedinger's Equation cannot be solved analytically for the anharmonic Hamiltonian operator and will require use of the numerical methods discussed above. As mentioned earlier, we will use the harmonic oscillator eigenfunctions as a basis for all Hamiltonian matrices and their eigenfunctions. We can then write the eigenfunctions  $\psi_n(x)$  of the anharmonic oscillator as a linear combination of the eigenfunctions of the harmonic oscillator

$$\psi_n(x) = \sum_{m=0}^{N-1} C_m u_m(x) \quad (22)$$

Note that  $N$  is the size of the basis, and therefore the dimension of the Hamiltonian matrix being solved, and therefore the number of equations being solved. From (22), the coefficients  $C_m$  are found by finding the eigenvectors of the anharmonic oscillator Hamiltonian and the eigenfunctions of the anharmonic oscillator are found using equation (22). Equation (22) is the equivalent of taking the dot product of the eigenvector of coefficients  $C_m$  with the vector of basis functions  $u_n$ .

We can now take the expectation values of the anharmonic oscillator Hamiltonian to generate matrix elements, finding

$$H_{nm} = [H_0]_{nm} + \lambda \langle u_n | \hat{x}^4 | u_m \rangle \quad (23)$$

The second term on the right hand side of (23) is the expectation value  $\langle \hat{x}^4 \rangle_{nm}$ . Because our basis is written in terms of harmonic oscillator eigenfunctions, we can determine  $\langle \hat{x}^4 \rangle_{nm}$  by use of the raising and lowering operators  $a^+$  and  $a^-$ . These operators are defined by  $a^+ u_n = \sqrt{n+1} u_{n+1}$

and  $a^- u_n = \sqrt{n} u_{n-1}$ . Additionally, the raising and lowering operators are related to the position operator by  $\hat{x} = (a^+ + a^-)/\sqrt{2}$ , which we can use to find  $\langle \hat{x}^4 \rangle_{nm}$ . After tedious calculations we find,

$$\begin{aligned}\langle \hat{x}^4 \rangle_{nm} = & \frac{1}{4}(6n^2 + 6n + 3)\delta_{nm} + \sqrt{(n+1)(n+2)}(n + \frac{3}{2})\delta_{n,m-2} \\ & + \sqrt{(n-1)n}(n - \frac{1}{2})\delta_{n,m+2} + \frac{1}{4}\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{n,m-4} \\ & + \frac{1}{4}\sqrt{(n-3)(n-2)(n-1)n}\delta_{n,m+4}\end{aligned}\quad (24)$$

Thus, our anharmonic oscillator Hamiltonian matrix  $\overleftrightarrow{H}$  is constructed by,

$$\begin{aligned}H_{nm} = & (n + \frac{1}{2})\delta_{nm} + \lambda(\frac{1}{4}(6n^2 + 6n + 3)\delta_{nm} + \sqrt{(n+1)(n+2)}(n + \frac{3}{2})\delta_{n,m-2} \\ & + \sqrt{(n-1)n}(n - \frac{1}{2})\delta_{n,m+2} + \frac{1}{4}\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{n,m-4} \\ & + \frac{1}{4}\sqrt{(n-3)(n-2)(n-1)n}\delta_{n,m+4})\end{aligned}\quad (25)$$

The SciPy function `eigh()` constructs a matrix  $\mathcal{C}$  of coefficients  $C_{mn}$ , where each column represents an eigenvector for the matrix  $\overleftrightarrow{H}$ . The first column represents the ground state  $n = 0$ , the second column represents the first excited state  $n = 1$ , and so on. As mentioned earlier, the eigenfunctions for the anharmonic oscillator can be found by using equation (22) for a given column of  $\mathcal{C}$ , or by taking the dot product of the vector of basis functions  $u_n$  with the desired column of  $\mathcal{C}$ .

### 2.3 Double-Well Potential

The double-well potential is given by  $V(x) = -4x^2 + x^4$  and the Hamiltonian operator is given by

$$\hat{H} = \hat{H}_0 - \frac{9}{2}\hat{x}^2 + \hat{x}^4 \quad (26)$$

The problem of the double-well potential is similar to that of the anharmonic oscillator potential in that Schroedinger's Equation cannot be solved analytically for the given Hamiltonian operator. However, also like the anharmonic oscillator problem we can write the eigenfunctions of the double-well potential as a linear combination of harmonic oscillator eigenfunctions using equation (22). Taking the expectation value of double-well potential operator, and once again using raising/lowering operators, with the relation  $\hat{x} = (a^+ + a^-)/\sqrt{2}$ , to find the expectation values of the  $\hat{x}^2$  and  $\hat{x}^4$  terms, we find the Hamiltonian matrix elements determined by

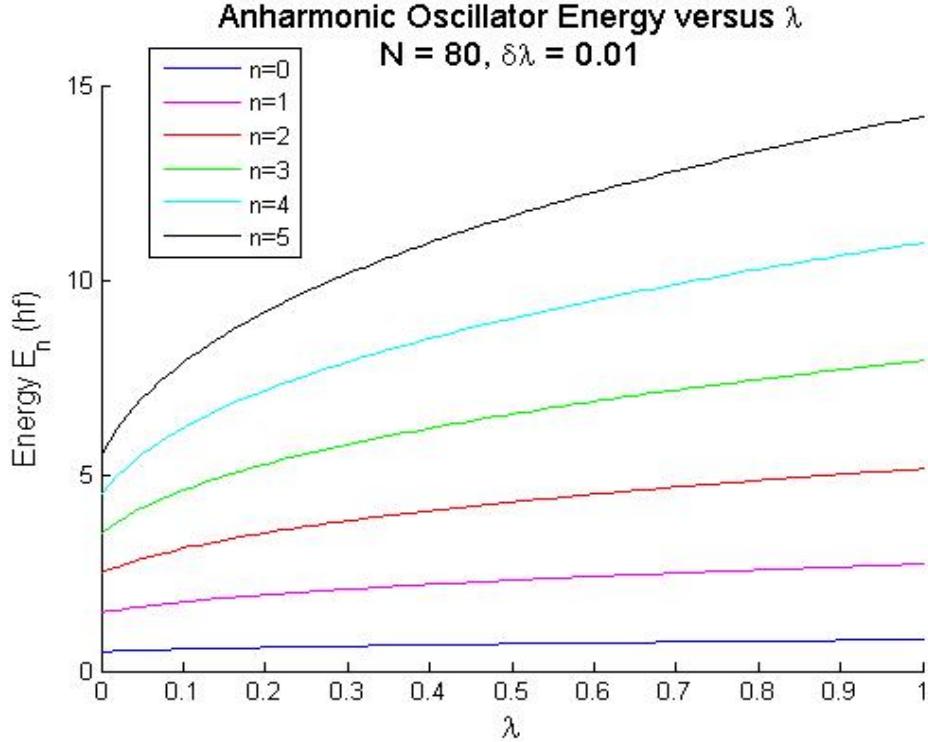
$$\begin{aligned}H_{nm} = & (n + \frac{1}{2})\delta_{nm} - \frac{9}{2}((n + \frac{1}{2})\delta_{nm} + \frac{1}{2}\sqrt{(n+1)(n+2)}\delta_{n,m-2} + \frac{1}{2}\sqrt{(n-1)n}\delta_{n,m+2}) \\ & + \frac{1}{4}(6n^2 + 6n + 3)\delta_{nm} + \sqrt{(n+1)(n+2)}(n + \frac{3}{2})\delta_{n,m-2} \\ & + \sqrt{(n-1)n}(n - \frac{1}{2})\delta_{n,m+2} + \frac{1}{4}\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{n,m-4} \\ & + \frac{1}{4}\sqrt{(n-3)(n-2)(n-1)n}\delta_{n,m+4}\end{aligned}\quad (27)$$

From the above equation we can generate the matrix  $\overleftrightarrow{H}$  and solve for the eigenvalues and eigenvectors using the SciPy function `eigh()`, as before. Once again the dot product is taken with the desired eigenvector of  $\overleftrightarrow{H}$  and the vector of basis functions  $u_n$  to find the eigenfunctions for the double-well potential.

### 3 Results

#### 3.1 Anharmonic Oscillator Energy Levels $E_n(\lambda)$

In this problem we were to solve anharmonic oscillator matrix eigenvalue problem and plot the first four, or more, energy levels over a range of  $\lambda$  values  $0 \leq \lambda \leq 1$ . That is to say we were to plot low energy levels as a function of the anharmonic potential strength  $\lambda$ :  $E_n(\lambda)$ . Our solution plot of the first six states (up to  $n = 5$ ) is shown below,

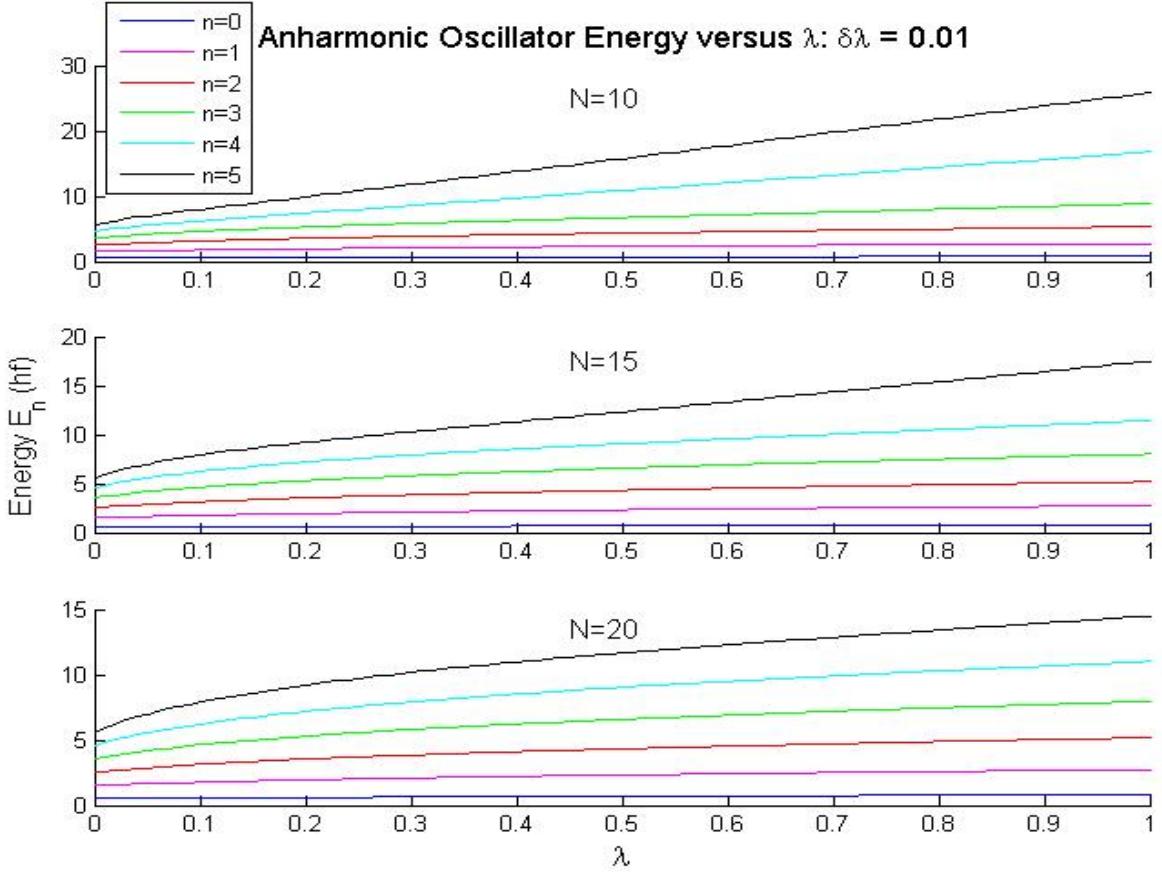


**Figure 1:** Energy levels up to  $n = 5$  as a function of the anharmonic potential strength  $\lambda$  for  $N = 80$  linear equations and a lambda step size  $\delta\lambda = 0.01$ . The large amount of equations make these energy values fairly accurate.

The above result for the first six energy levels of the anharmonic oscillator as a function of the anharmonic oscillator potential strength  $\lambda$  has some interesting characteristics. First of all, notice how each energy level  $E_n$  has a discontinuous jump from the previous energy level. This is a result of the quantization of energy mentioned earlier, and is an indication that our result is correct. A more interesting result, however, is the potential strength  $\lambda$  and its effects on the energy levels. Notice how near  $\lambda = 0$  the energy levels appear evenly spaced by a discrete value of  $n = 1$ . This is because at  $\lambda = 0$ , the energy levels are entirely equivalent with those of the harmonic oscillator, whose energy eigenvalues are  $E_n = n + \frac{1}{2}$ . As  $\lambda$  is increased the energy in all levels begins to increase from the base values given by the harmonic oscillator energy eigenvalues. For high energy levels,  $n = 5$  in particular, the energy appears to increase as  $E_n(\lambda) \propto \sqrt{\lambda}$  while the lower energy levels such as  $n = 0$  do not appear to increase at all. Though all energy levels are indeed increasing with the potential strength  $\lambda$ , as they should, the high energy levels appear to increase more than the lower ones. This is due to the anharmonic terms in the Hamiltonian matrix, equation (25), and their dependence on the  $\sqrt{n}$ . These square-root terms are not significant for lower energy levels, and in fact many of them are zero for  $n = 0$ . Therefore as  $\lambda$  is increased these already small terms do not greatly increase the value of the energy. For higher energy levels, however, the square-root terms are significant and as the strength of the anharmonic potential is increased, so too does its

dependence on the  $\sqrt{n}$  in the Hamiltonian matrix become more and more evident.

The result shown in Fig. 1 used a Hamiltonian matrix dimension of  $N = 80$ , or  $N = 80$  linear equations needed to be solved. More equations leads to greater accuracy in the result for numerical methods used. This is demonstrated in the following plot.

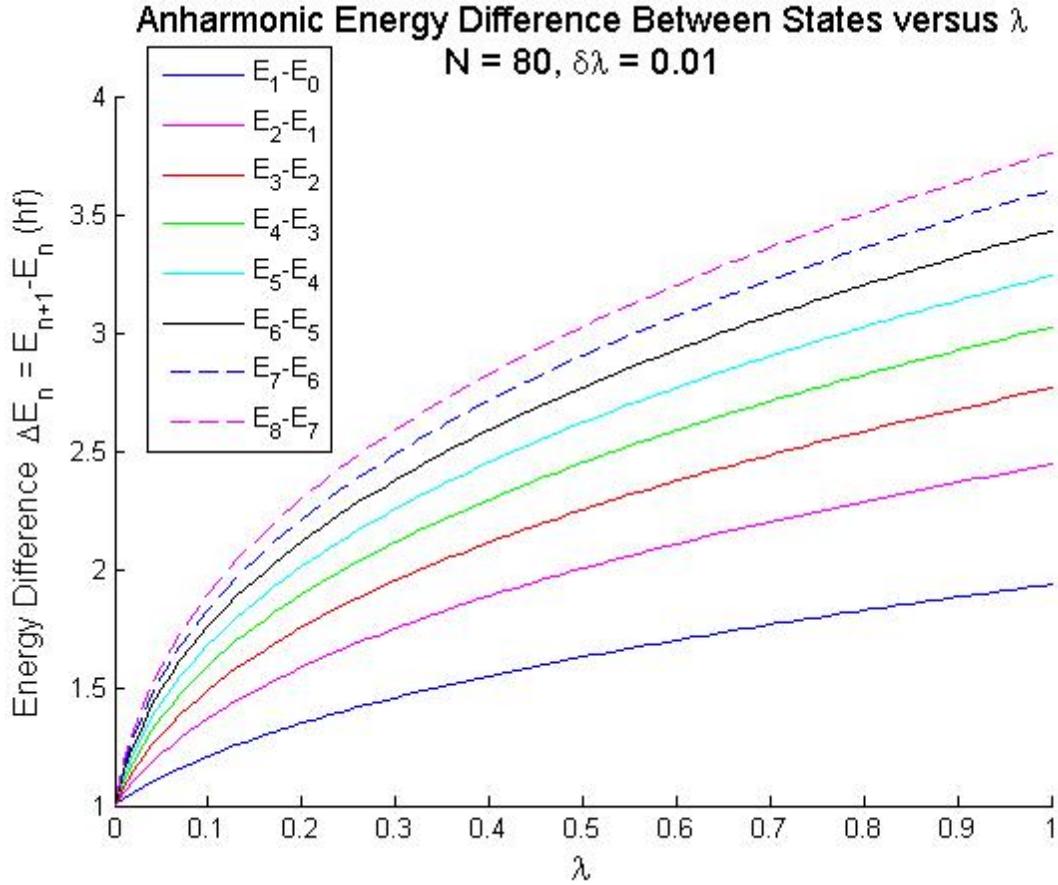


**Figure 2:** Energy levels up to  $n = 5$  as a function of the anharmonic potential strength  $\lambda$  for  $N = 10$ ,  $N = 15$ , and  $N = 20$ . Notice how the  $N = 20$  results appear close to those in Fig. 1 while the  $N = 10$  and  $N = 15$  grow faster with  $\lambda$  than  $N = 20$  AND  $N = 80$ .

Figure 2 contains three plots of the first six energy level for relatively low values of  $N$  compared to Fig. 1. The error incurred in the energy growth is most noticeable for  $N = 10$ , where the energy clearly appears to grow linearly with  $\lambda$ ,  $E_n(\lambda) \propto \lambda$ , rather than with the square-root of  $\lambda$  as with  $N = 80$ . For  $N = 15$  the energy still appears to grow linearly for large values of  $\lambda$  but grows as  $\sqrt{\lambda}$  for small values of  $\lambda$ . This is due to the common remedy of multiplying a large number by a small number in order to counter any round-off error. By  $N = 20$ , the results appear consistent with our original result for  $N = 80$ .

Our final task for this problem was to plot the spacings between the levels as a function of  $\lambda$ :  $\Delta E_n(\lambda) = E_{n+1}(\lambda) - E_n(\lambda)$ . The plot for  $\Delta E(\lambda)$ , for  $N = 80$  equations up to  $n = 8$ , is shown in Figure 3 on the next page. Figure 3 shows more explicitly what was mentioned earlier, that for  $\lambda = 0$  the energy spacings between all energy levels is  $\Delta E_n(0) = 1$ . This is because the anharmonic potential has no effect on the energy eigenvalues or the eigenfunctions for that matter; the system is entirely equivalent to the quantum harmonic oscillator for  $\lambda = 0$ . Also mentioned before is the fact that the difference between energy levels increases as the energy levels increase. For example, in Figure 3 the greatest energy difference is for  $E_8 - E_7$  while the smallest if for  $E_1 - E_0$ . Once again, this is due to the anharmonic potential's dependence on  $\sqrt{n}$  terms in the Hamiltonian matrix,

which are not as significant for low energy levels  $n$ , albeit the energy difference between the ground state and first excited state is nearly doubled for  $\lambda = 1$ . As mentioned before, the energy spacings



**Figure 3:** Energy level spacings  $\Delta E_n(\lambda) = E_{n+1}(\lambda) - E_n(\lambda)$  for  $N = 80$  equations and up to the  $n = 8$ . Notice how as  $\lambda$  approaches zero the energy spacings converge to one but diverge as  $\lambda$  approaches one.

are clearly proportional to the  $\sqrt{\lambda}$  because of the square-root anharmonic terms in the Hamiltonian matrix, which are most significant for large  $n$ . Finally, though the energy spacing between energy levels is increasing with larger values of  $n$ , the rate at which the spacing is growing appears to be decreasing, and approaching some limit. If the energy spacings do in fact increase like,

$$\Delta E_n(\lambda) \propto \sqrt{\lambda} \quad (28)$$

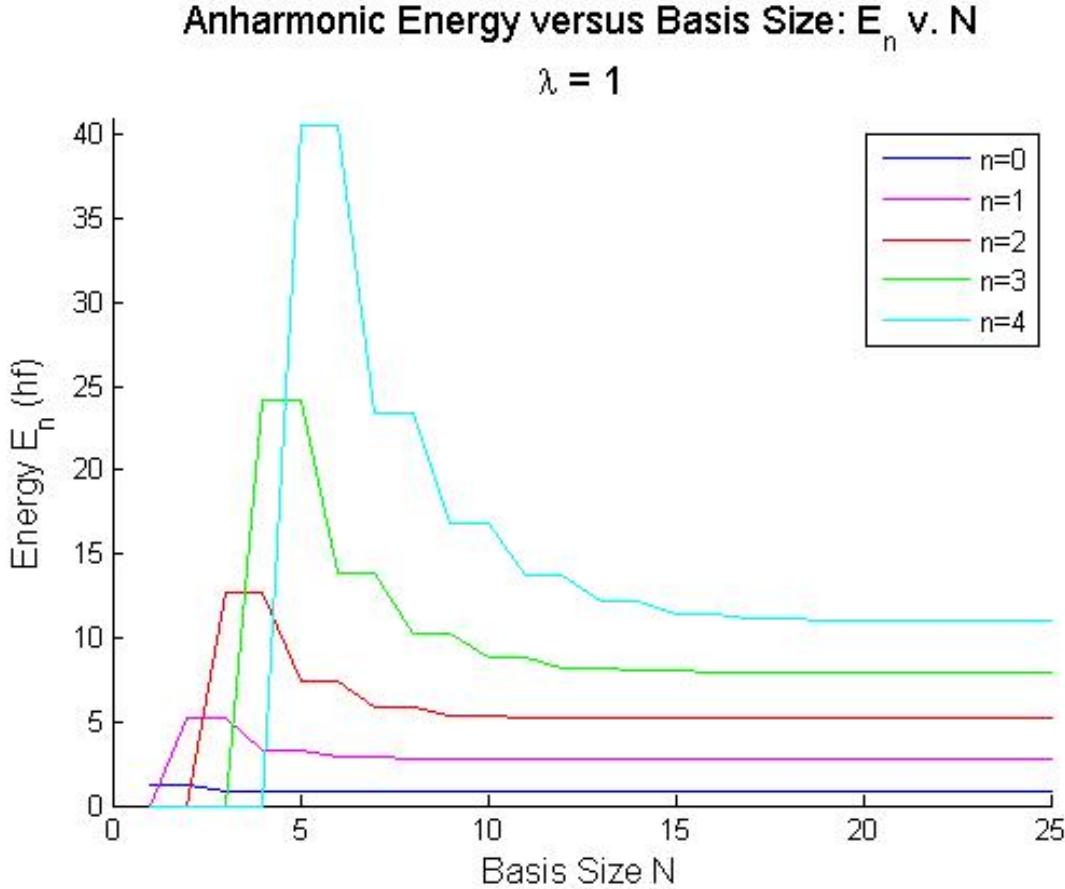
then it would also make sense that the energy spacings increase like

$$\frac{d\Delta E_n(\lambda)}{d\lambda} \propto \frac{1}{2\sqrt{\lambda}} \quad (29)$$

which shows that the rate at which the energy spacings increase decreases with larger  $\lambda$ , and therefore larger  $n$  as well.

### 3.2 Convergence of Numerical Method with respect to N

For this problem we are to check the convergence of the numerical method used, in this case the SciPy function `eigh()`, with respect to the basis size  $N$ , or the number of linear equations. To accomplish this, we plot the first few energy levels  $n$  as a function of  $N$ ,  $E_n(N)$ , for  $\lambda = 1$ . The result for the first five energy levels is shown below,



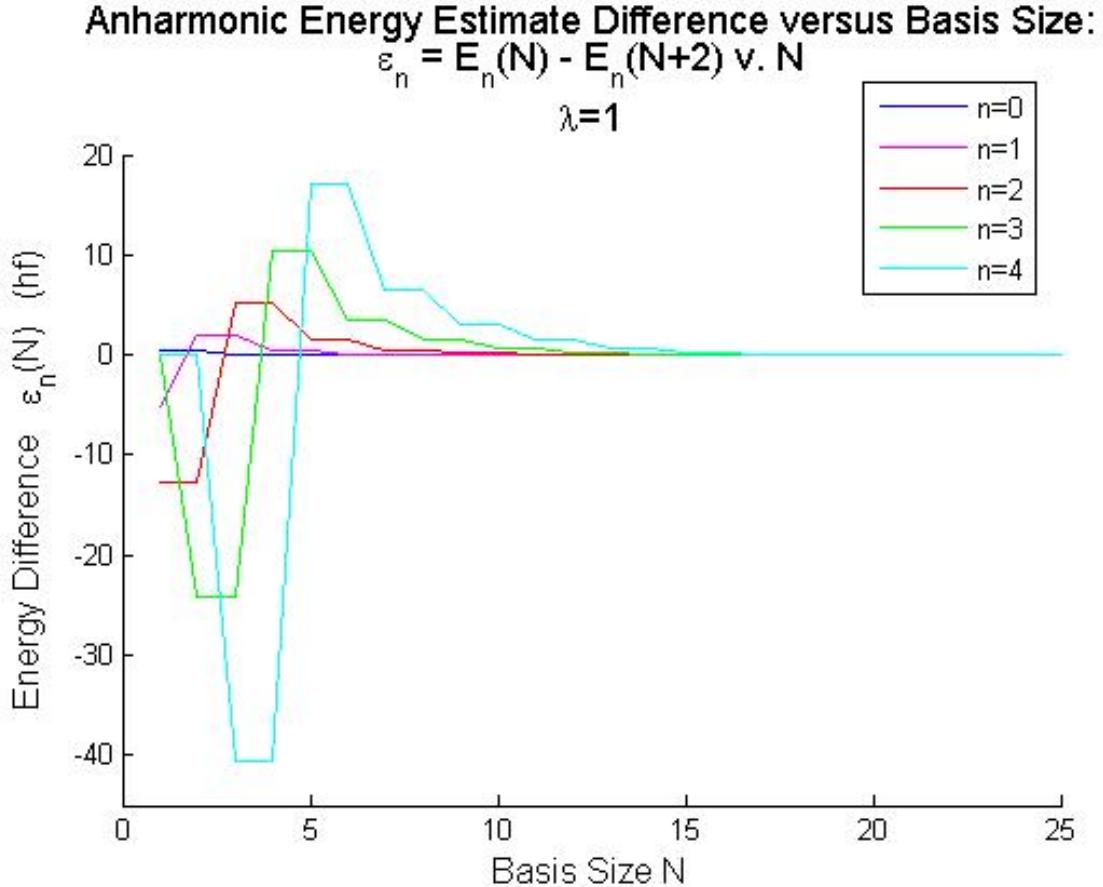
**Figure 4:** The first five energy levels of the anharmonic oscillator as a function of the basis size  $N$  with  $\lambda = 1$ . Note that the energy values appear to converge to their actual values like  $\mathcal{O}(N^2)$ . The algorithm used to produce this result is `eigh()` from SciPy.

Notice how each curve for a higher energy level  $n$  must begin at a higher basis size  $N$ . This is simply because not enough basis functions, or equations, are being used to calculate higher energy states, resulting in zero values of energy until enough basis functions are used. For example, the  $n = 0$  state only requires a basis of  $N = 1$ , but the fifth state  $n = 4$  requires a basis of at least  $N = 5$ .

From inspecting Fig. 4, it appears as though once there are non-zero energy values for a given state, the energy converges to its actual value at a rate of  $\mathcal{O}(N^2)$ . This is consistent with the nominal quadratic scale rate of the algorithms used to solve eigenvalue problems, where the function `eigh()` from SciPy was used to generate Fig. 4. Clearly, the  $n = 0$  energy state converges rather quickly, converging in what looks like an increase of  $N_0 + 1$  in the basis size from its first non-zero value at  $N_0$ . The  $n = 1$  state appears to converge in a  $N_0 + 4$  increase in basis size, the  $n = 2$  state appears to converge in a  $N_0 + 9$  increase in basis size, the  $n = 3$  state appears to converge in a  $N_0 + 12$  increase in basis size, and the  $n = 4$  state appears to converge in at least a  $N_0 + 15$  increase in basis size. These increases in basis size required for energy levels to converge clearly illustrate a

convergence that does not exceed  $\mathcal{O}(N^2)$ .

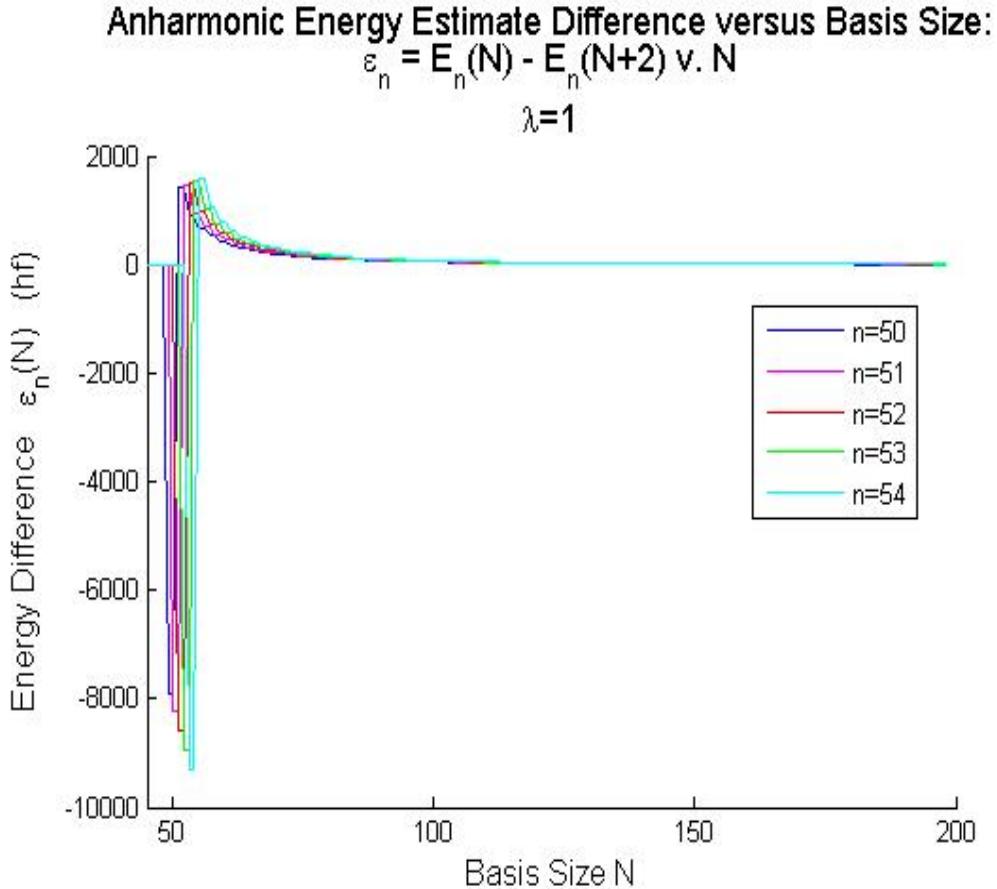
To illustrate this convergence more clearly, we also plotted the difference between two consecutive estimates, given by  $\epsilon_n = E_n(N) - E_n(N + 2)$  for  $\lambda = 1$ . This result, for the first five energy states, is shown in Figure 5 below.



**Figure 5:** The difference between two consecutive measurements,  $\epsilon_n = E_n(N) - E_n(N + 2)$ , for the first five energy levels of the anharmonic oscillator as a function of the basis size  $N$  with  $\lambda = 1$ . Note that the energy values appear to converge to zero like  $\mathcal{O}(N^2)$ . The algorithm used to produce this result is `eigh()` from SciPy.

From Fig. 5 above we more or less see the same result as in Fig. 4 except all difference in estimates for a given energy level converge to  $\epsilon = 0$ . This makes things somewhat clearer as to how many additional basis functions are needed for convergence, but they appear to closely follow the same increases specified for Fig. 4. A more interesting plot is the difference between two consecutive estimates for large values of energy levels  $n$ . This plot is shown in Figure 6 on the next page, where we have plotted the energy levels  $n = 50$  through  $n = 54$ .

Notice how, like Fig. 5, these energy levels also appear to converge to zero with the rate  $\mathcal{O}(N^2)$ . But because the smallest energy level difference plotted in Fig. 6 is for  $n = 50$ , we should not expect the energy level differences to fully converge to zero as about  $N \approx 2500$  basis functions are required for the  $n = 50$  state alone to converge. Indeed if you look closely at the plot around  $N = 200$ , the energy level differences  $\epsilon_n$  appear very close to zero, but not quite converged to zero. The maximum basis size used,  $N = 200$ , is probably close enough for any practical purposes, however. Figure 6 illustrates the considerations of accuracy and time that must be taken into account when using numerical methods since it is clearly unnecessary in this case to increase the basis size to  $N = 2500$  when an acceptably accurate solution can be achieved with less than a tenth of the basis size.



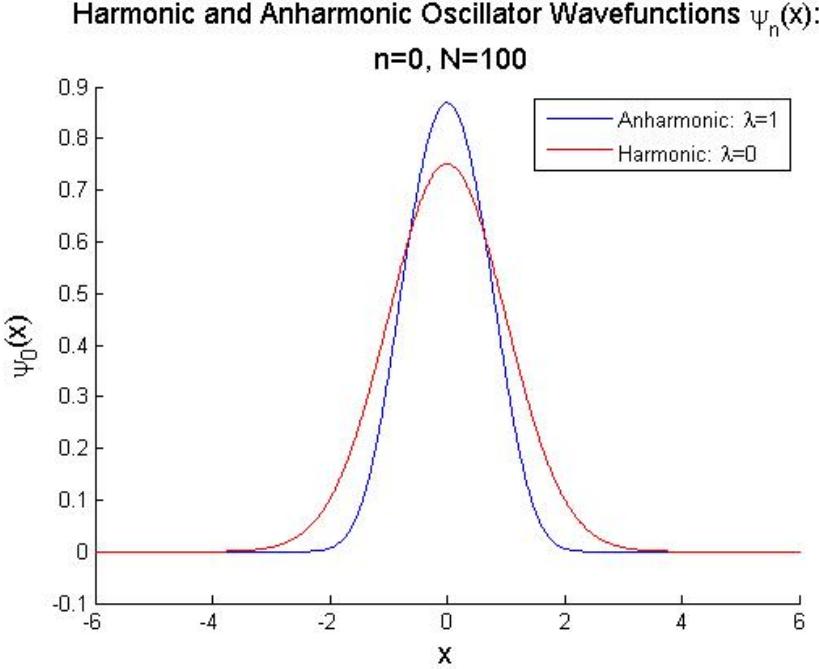
**Figure 6:** The difference between two consecutive measurements,  $\epsilon_n = E_n(N) - E_n(N + 2)$ , for the energy levels  $n = 50$  through  $n = 54$  of the anharmonic oscillator as a function of the basis size  $N$  with  $\lambda = 1$ . Note that the energy values still appear to converge to zero like  $\mathcal{O}(N^2)$ , however these energy levels do not appear to fully converge since a basis size of  $N \approx 2500$  is required.

### 3.3 Harmonic and Anharmonic Oscillator Eigenfunctions

For this problem we are to compare the first few eigenfunctions of the harmonic oscillator,  $\lambda = 0$ , with those of the anharmonic oscillator,  $\lambda = 1$ . The first two eigenfunctions  $\psi_n(x)$  are shown below, both of which were calculated using a basis of  $N = 100$ .

One of the most obvious differences between the harmonic and anharmonic eigenfunctions in the ground state  $n = 0$  is the different amplitudes for  $\psi_0(x)$ . Clearly, the anharmonic eigenfunction has a greater amplitude, about  $\psi_0(x) = 0.9$ , than the harmonic eigenfunction, which has an amplitude of about  $\psi_0(x) = 0.75$ . Additionally, the width of the wave packet, or spike, for the anharmonic oscillator eigenfunction is narrower, with a max width of about  $\Delta x = 4$ , than that of the harmonic oscillator which has a max width of about  $\Delta x = 8$ . Because the amplitude of an eigenfunction is related to the probability and the width of the wave packet is related to the standard deviation of the position operator  $\hat{x}$ , the differences between the anharmonic and harmonic oscillators can be explained in statistical and physical terms.

Recall that the potential, and therefore the Hamiltonian operator, of the anharmonic oscillator differs from that of the harmonic oscillator only by the addition of the term  $\lambda x^4$ . This extra term in the anharmonic oscillator potential increases the restoring force of the oscillation about  $x = 0$  because the additional anharmonic term is positive and symmetric about  $x = 0$ . The particle subject to the anharmonic potential can be thought of as being pulled more strongly back towards zero



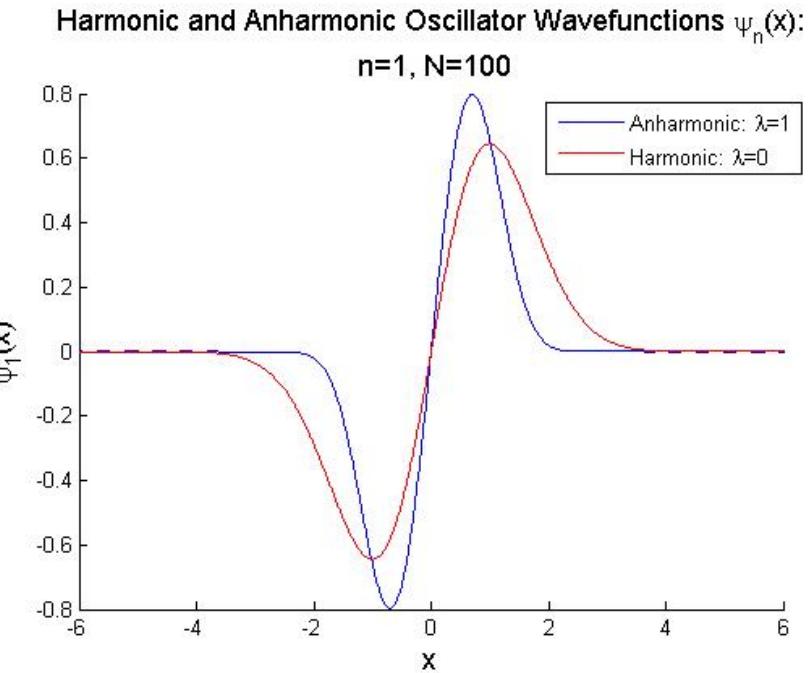
**Figure 7:** Eigenfunctions, or wavefunctions, for ground state of the harmonic and anharmonic oscillators with a basis of size  $N = 100$ .

than the harmonic oscillator. Consequently, the anharmonic oscillator is found at smaller  $|x|$  values compared to the harmonic oscillator because the strong restoring potential reduces the particle's displacement about  $x = 0$ . This has the effect of both increasing the amplitude of the anharmonic oscillator and reducing the width of the wave packet because the anharmonic oscillator is more likely to be found a smaller values of  $|x|$  than the harmonic oscillator. This increases the probability of the anharmonic oscillator for small  $|x|$ , thereby increasing the amplitude of its wave function, and decreases the uncertainty that the anharmonic oscillator will be found outside a small  $|x|$  range, thereby decreasing the wave packet width and subsequently the standard deviation of  $\hat{x}$  for the anharmonic oscillator.

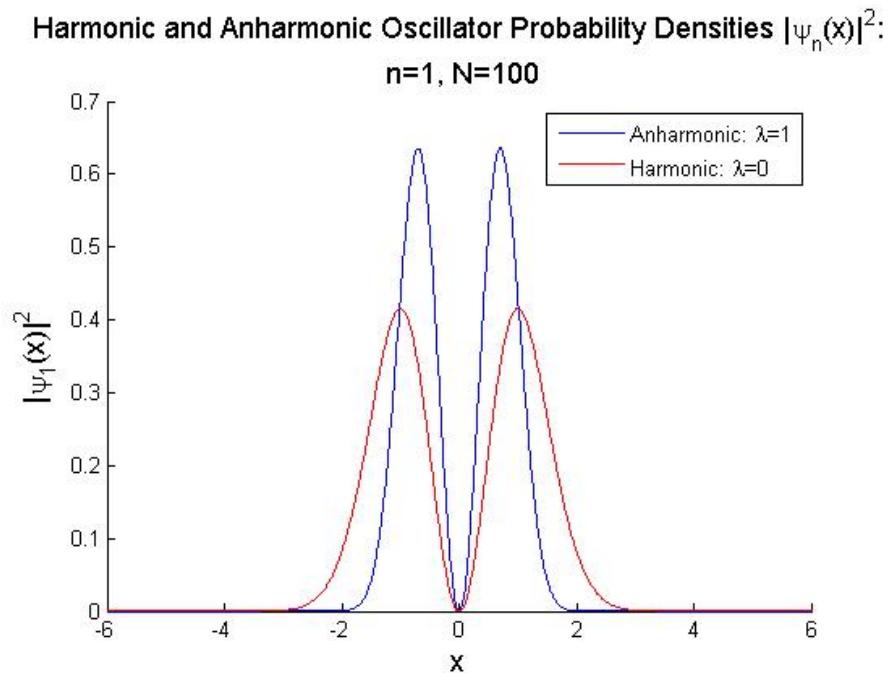
Figure 8 below are the eigenfunctions of the anharmonic and harmonic oscillators for the first excited state  $n = 1$ . The figure shares the same traits and Fig. 7, in particular the anharmonic oscillator eigenfunction having larger amplitudes and a narrower wave packet width than the harmonic oscillator eigenfunctions. However, because the state is excited, both oscillators have greater energy which allows them to not have a resonant peak about  $x = 0$  as in Fig. 7. If we look at the probability density of the first excited state for both oscillators the physical interpretation and differences becomes somewhat clearer.

From the probability densities of the harmonic and anharmonic oscillators in Fig. 9, we can now clearly see that excitation in energy creates two, symmetric resonant peaks about  $x = 0$  and that both oscillators now have a probability of being found at  $x = 0$  of zero. Regardless, the anharmonic oscillator has larger amplitudes and a narrower width than the harmonic oscillator about  $x = 0$ , indicating that the anharmonic oscillator is more likely to be found at smaller  $|x|$  values than the harmonic oscillator, regardless of the energy state.

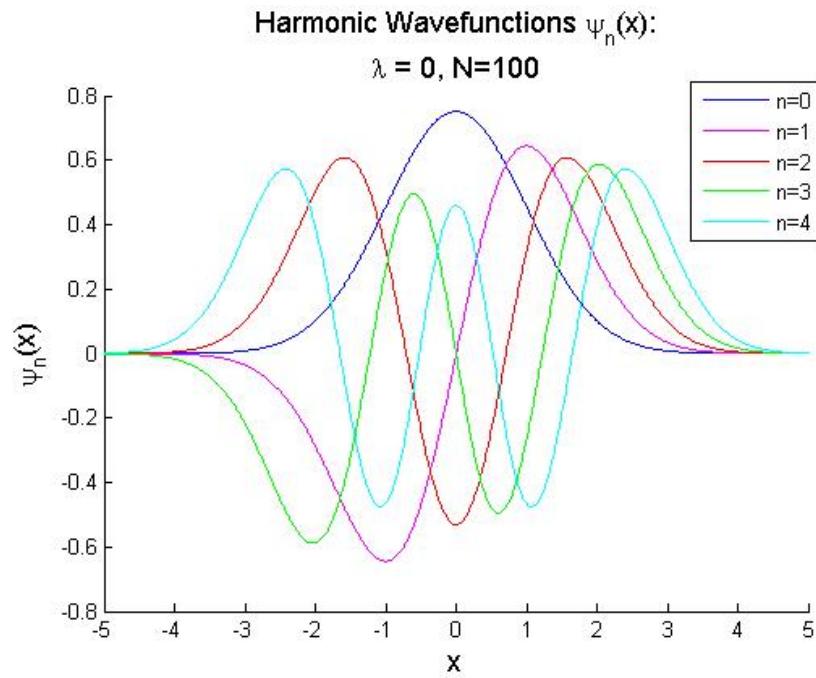
This is demonstrated more fully in Figures 10 and 11, which are the first five eigenfunctions for the harmonic and anharmonic oscillators, respectively. The anharmonic oscillator resembles the harmonic oscillator in shape for every energy level, but the stronger anharmonic potential keeps the anharmonic oscillator more tightly centered, and more likely to be found, about  $x = 0$ .



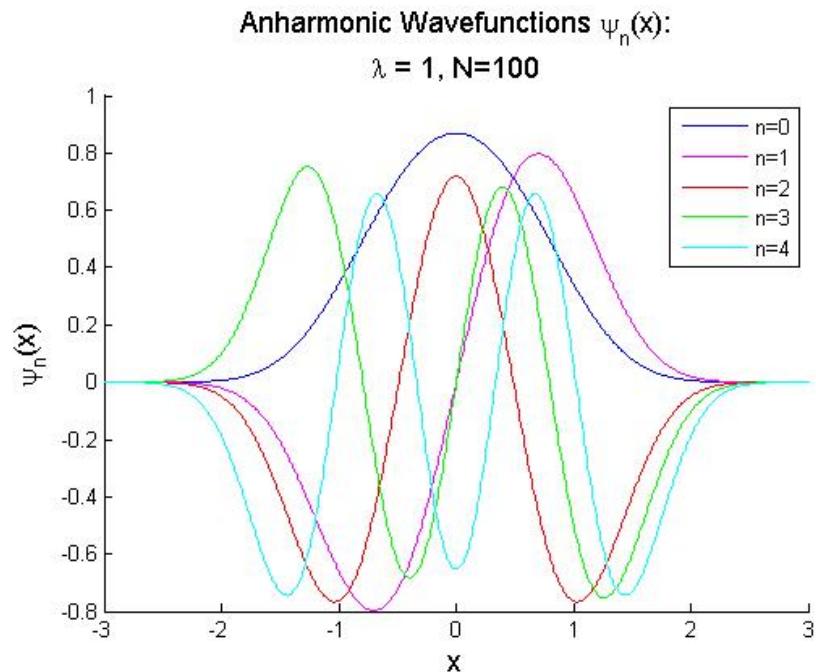
**Figure 8:** Eigenfunctions, or wavefunctions, for the first excited state of the harmonic and anharmonic oscillators with a basis of size  $N = 100$ .



**Figure 9:** Eigenfunctions, or wavefunctions, for the first excited state of the harmonic and anharmonic oscillators with a basis of size  $N = 100$ .



**Figure 10:** Eigenfunctions, or wavefunctions, for the first five states of the harmonic oscillator with a basis of size  $N = 100$ . Notice the maximum width of the wave packets for each state



**Figure 11:** Eigenfunctions, or wavefunctions, for the first five states of the anharmonic oscillators with a basis of size  $N = 100$ . Notice the maximum width of the wave packets for each state and how it is narrower than for the harmonic oscillators in Figure 10.