

# Workshop: Approximating energies and wave functions

## Quantum aspects of physical chemistry

<http://quantum.bu.edu/PLTL/6/6.pdf>  
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We have learned how to find wave functions and energies by adjusting the total energy so that the wave function decays to zero in forbidden regions of infinite width or infinite potential energy. In numerical applications of quantum mechanics in chemistry, an alternative, flexible method of solving the Schrödinger equation is to approximate the wave function for a particular system in terms of those for a similar, so-called model system. A very nice feature of this approach is that the accuracy of the approximation can be systematically improved, by increasing the number of model wave functions used in the approximation. In this workshop we'll explore this method, for the example of a particle confined to an infinite well with a sloping bottom. The model system will be the corresponding infinite well with a flat bottom.

### Part 1

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#### ■ A curved infinite well

The goal of this workshop is to determine the wave function,  $\Psi_1$ , and energy,  $E_1$ , for the ground state of a particle in an infinite well that has a bottom that curves up toward the right wall. Here is a plot of the curved infinite square well, and the corresponding flat infinite square well.

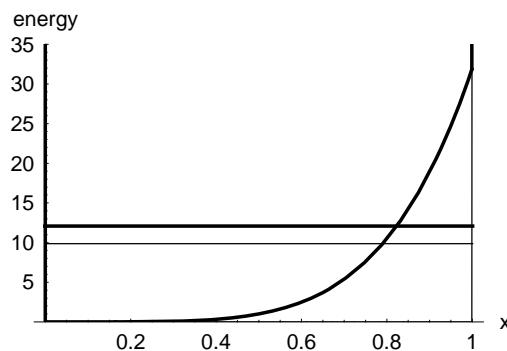


Figure 1. Distorted infinite square well potential energy (thick line) and corresponding undistorted infinite well potential energy (thin line). The thick horizontal line is the ground state energy, 12.08, of the distorted infinite well and the thin horizontal line is the ground state energy, 9.869, of the undistorted infinite well. Energy and length are in dimensionless units.

The distortion is  $(2x)^5$  in dimensionless units.

1. We know that the ground state energy of a particle of mass  $m$  confined in a infinite square well of width  $L$  is  $\hbar^2 / (8 m L^2)$ . If we assume the particle is an electron, determine the units of energy if the width is  $2.0 \text{ \AA}$ . Answer  $1.5 \times 10^{-18} \text{ J}$ .
2. Show that this means that the distorted well potential energy rises from 0 J at the left wall to  $48 \times 10^{-18} \text{ J}$  at the right wall.

## ■ Exact ground state energy wave function

So that we have a point of comparison, we can determine the exact energy and wave function of the distorted and undistorted well by solving the curvature form of the Schrödinger equation, by adjusting the total energy so the wave function has a single loop and decays to zero at each edge of the infinite well.

The result is that the ground state energy of the distorted square well,  $E_1 = 12.1$ , is about 20% higher than that of the undistorted well,  $E_0 = 9.9$ .

3. Explain why the ground state energy of the distorted well must be higher than that of the undistorted well.

Here is a plot of the ground state wave function,  $\Psi_1(x)$  (thick curve), of the distorted and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$  (thin curve), of the undistorted well.

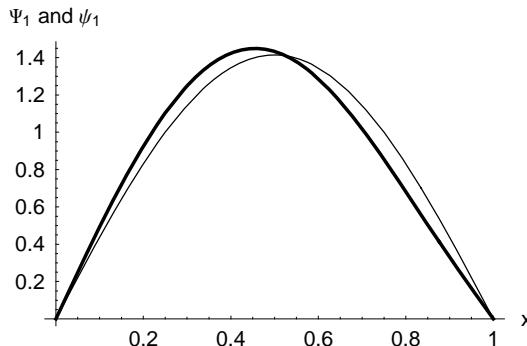


Figure 2. Ground state wave function,  $\Psi_1(x)$  (thick curve), of the distorted well and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$  (thin curve), of the undistorted well.

Here is a plot of the curvature,  $d^2\Psi_1/dx^2$ , of the exact ground state wave function.

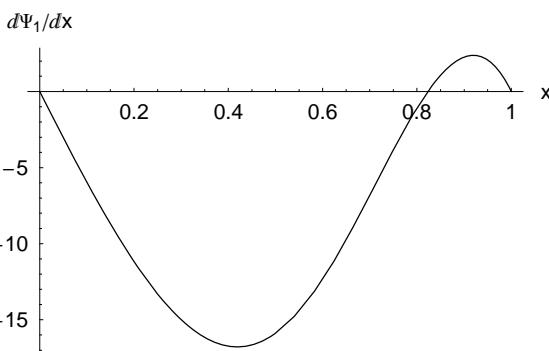


Figure 3. Curvature,  $d^2\Psi_1/dx^2$  of the exact ground state wave function.

4. From the plot of the potential energy and the total energy, does the distorted well have a forbidden region *between* the infinite potential energy wall at  $x = 0$  and  $x = 1$ ? If so,

indicate the corresponding classical turning point and the inflection point in the wave function.

Here is a plot of the difference,  $\Psi_1(x) - \psi_1(x)$ , between the exact and the model system ground state wave functions.

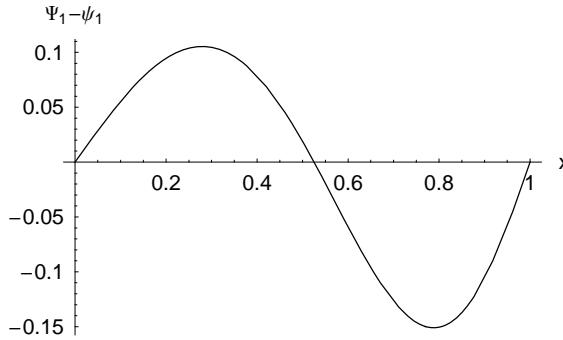


Figure 4. Wave function difference,  $\Psi_1(x) - \psi_1(x)$ .

5. Account for the difference in these two wave functions, in terms of the difference in the corresponding potential energies.

## ■ First order approximation to energy

An alternative to using the curvature form of the Schrödinger equation to determine the energy and wave function of the distorted well, is to solve for these quantities by expanding in the basis of wave functions of the undistorted well. The general form of this expansion for wave function,  $\Psi_\alpha$ , of the distorted well with  $\alpha$  loops and energy  $E_\alpha$  is

$$\Psi_\alpha = \sum_j \psi_j c_{j,\alpha}.$$

The simplest approximation to the ground state wave function,  $\Psi_1$ , of the distorted well is to include just a single term,

$$\Psi_1 = \sum_j \psi_j c_{j,1} \approx \psi_1 c_{1,1}.$$

Since the wave functions of the undistorted well are normalized, we can ensure that  $\Psi_1$  is normalized by setting the coefficient  $c_{1,1}$  equal to one. This means that at this level of approximation, we assume the distortion in the potential energy *does not change the wave function* from that of the undistorted potential.

Once we have an approximation to the wave function, we can use the Schrödinger equation to determine the corresponding approximation to the energy.

$$H \Psi_1 \approx H \psi_1 \approx E_1 \psi_1$$

Here is how to work with this approximate Schrödinger equation. Because  $\psi_1$  is not really an eigenfunction of  $H$ , the result of operating with  $H$  on  $\psi_1$  will *not* be proportional to  $\psi_1$  and so we have no proportionality that we can use to identify the approximate eigenvalue.

Instead, what we can do is multiply both sides of the second approximate equality by  $\psi_1^*$  and then integrate over the well. The result is

$$\int_0^1 \psi_1(x)^* H(x) \psi_1(x) dx \approx E_1$$

That is, the first approximation to the energy is

$$E_1 \approx E_1^{(1)} = \int_0^1 \psi_1(x)^* H(x) \psi_1(x) dx$$

To evaluate the integral it is very helpful to express the Hamiltonian in terms of the Hamiltonian,  $H^{(0)}$ , of the undistorted potential, that is, to write  $H = H^{(0)} + (H - H^{(0)})$ . The difference  $H - H^{(0)}$  is called the *perturbation* to the undistorted hamiltonian.

6. Show that since the perturbation,  $H - H^{(0)}$ , between the distorted well and the undistorted well is the potential energy,  $(2x)^5$ , the first approximation to the energy can be expressed as

$$E_1^{(1)} = \epsilon_1 + \int_0^1 \psi_1(x)^* (2x)^5 \psi_1(x) dx$$

where we use the symbol  $\epsilon_j = j^2 \hbar^2 / (8mL^2)$  for the energies of the undistorted well.

7. The integral  $\int_0^1 \psi_1(x)^* (2x)^5 \psi_1(x) dx$  evaluates to 2.512. Evaluate, in dimensionless units, the first approximation to the energy of the distorted well. Answer: 12.38.

8. Evaluate the percentage error in the first approximation to the energy. Answer: 2.48%

## ■ Accuracy of the first order approximation to energy

The net result of the simplest, so-called *first order approximation* scheme is that we can estimate the ground state energy,  $E_1$ , of a system in terms of the energy,  $\epsilon_1$ , and ground state wave function,  $\psi_1$ , of a model system as

$$E_1 \approx \epsilon_1 + \int_0^1 \psi_1(x)^* (H - H^{(0)}) \psi_1(x) dx,$$

where the perturbation  $H - H^{(0)}$  is the operator corresponding to the difference between the actual system and the model system. In the example above,  $H - H^{(0)} = (2x)^5$ .

We have seen that this very simple approximation does a very good job in predicting the energy of the system, in that the error is only 2.48%. Let's see how this scheme works for a modified version of the distorted well.

9. Show that the first order estimate of the ground state energy of an infinite well with distorted potential energy  $H - H^{(0)} = (4x)^5$  is  $E_1 \approx E_1^{(1)} = 90.27$ .

The exact ground state energy is  $E_1 = 29.63$ . This means that now the percentage error is 502%! Indeed, the zero order energy—the energy of the undistorted potential, 9.86 units—is closer to the exact energy than is the first order approximation. Let's see if we can understand why now the error in the first order approximation to the energy is so much greater

Here is a plot of the new distorted potential energy and that of the undistorted well, together with the corresponding ground state energies, shown as horizontal lines.

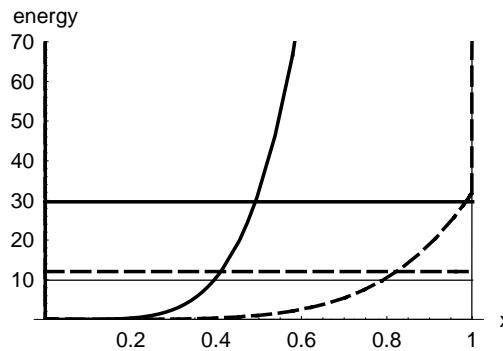


Figure 5. Modified (thick line) and original (thick, dashed line) distorted infinite square well potential energy and corresponding undistorted infinite well potential energy (thin line). The horizontal lines are the ground state energy, 29.63, of the modified distorted infinite well (thick line) and the ground state energy, 12.08, of the original distorted infinite well (thick, dashed line). The thin horizontal line is the ground state energy, 9.869, of the undistorted infinite well. Energy and length are in dimensionless units.

Here is a plot of the ground state wave function,  $\Psi_1(x)$  (thick curve), of the modified distorted well, and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$  (thin curve), of the undistorted well.

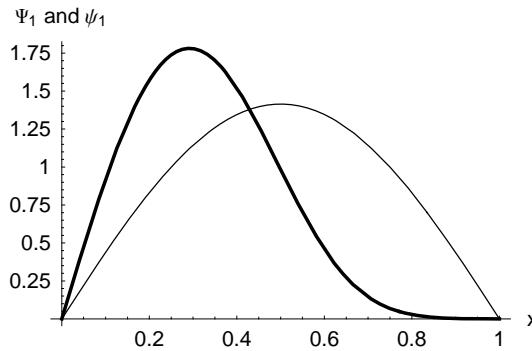


Figure 6. Ground state wave function,  $\Psi_1(x)$  (thick curve), of the modified distorted well, with potential energy  $(4x)^5$ , and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$  (thin curve), of the undistorted well.

10. From the plot of the potential energy and the total energy, does the modified distorted well have a forbidden region *between* the infinite potential energy wall at  $x = 0$  and  $x = 1$ ? If so, indicate the corresponding classical turning point and the inflection point in the wave function.
11. Compare the exact ground state wave function for the original distorted potential energy,  $(2x)^5$ , and the new distorted potential energy,  $(4x)^5$ . Based on your comparison can you anticipate when the first order approximation to the energy will work well and when it will not?

## ■ Second order approximation to the energy; first order approximation to the wave function

The next simplest approximation to the ground state wave function,  $\Psi_1$ , of the distorted well is to include two terms in the expansion of the distorted well wave function,

$$\Psi_1 = \sum_j \psi_j c_{j,1} \approx \psi_1 c_{1,1} + \psi_2 c_{2,1}.$$

As before, once we have an approximation to the wave function, we can use the Schrödinger equation to determine the corresponding approximation to the energy,

$$H\Psi_1 \approx H\{\psi_1 c_{1,1} + \psi_2 c_{2,1}\} \approx E_1 \{\psi_1 c_{1,1} + \psi_2 c_{2,1}\}.$$

At this point, though, we have to proceed differently, since we do not know the relative contributions of the two undistorted wave functions, that is, since we do not know the expansion coefficients  $c_{1,1}$  and  $c_{2,1}$ .

The first step is to transform the Schrödinger equation into two algebraic equations, that we can then try to use to determine the unknown expansion coefficients. One of the "secret handshakes" of quantum mechanics is the way to carry out the transformation to algebraic equations. This is done by first multiplying the approximate Schrödinger equation by  $\psi_1^*$  and then integrating over the potential energy well.

12. Show that the result of these steps is

$$H_{1,1} c_{1,1} + H_{1,2} c_{2,1} \approx E_1 c_{1,1},$$

$$\text{in terms of the matrix elements } H_{j,k} = \int_0^1 \psi_j(x)^* H \psi_k(x) dx.$$

In a similar way we can get another algebraic equation using  $\psi_2^*$ ,

$$H_{2,1} c_{1,1} + H_{2,2} c_{2,1} \approx E_1 c_{2,1}.$$

The next step is to get numerical values for the *matrix elements*  $H_{j,k}$ . To do this we need the integrals

$$\int_0^1 \psi_1(x)^* (2x)^5 \psi_2(x) dx = -2.920$$

and

$$\int_0^1 \psi_2(x)^* (2x)^5 \psi_2(x) dx = 4.397,$$

where the values are in dimensionless energy units.

13. Determine the values of  $H_{1,1}$ ,  $H_{1,2}$ ,  $H_{2,1}$  and  $H_{2,2}$ , in dimensionless energy units.  
Answer: 12.38, -2.92, -2.92 and 43.87.

14. Use these values of  $H_{j,k}$ , to reduce the Schrödinger equation to the two algebraic equations

$$12.38 c_{1,1} - 2.92 c_{2,1} = E_1 c_{1,1},$$

and

$$-2.92 c_{1,1} + 43.87 c_{2,1} = E_1 c_{2,1}.$$

## ■ Ensuring that we can solve the approximation: The secular equation and the second order approximation to the energy

Using matrix notation, the algebraic equations of the second order approximation can be written compactly as

$$(\mathbf{H} - E_\alpha \mathbf{I}) \mathbf{c} = \begin{pmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2} \end{pmatrix} - E_\alpha \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{pmatrix} = \begin{pmatrix} 12.38 - E_\alpha & -2.92 \\ -2.92 & 43.87 - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{pmatrix} = 0.$$

15. Carry out the matrix multiplication in the last equality to show that this equation is equivalent to the two algebraic equations, with  $E_1$  replaced by  $E_\alpha$  and the corresponding second index on the expansion coefficients by  $\alpha$ .

We'll see in a moment why we have replaced  $E_1$  with the more general symbol  $E_\alpha$ , and correspondingly introduced the subscript  $\alpha$  in the expansion coefficients.

If we could find the inverse matrix,  $(\mathbf{H} - E_\alpha \mathbf{I})^{-1}$ , then since  $(\mathbf{H} - E_\alpha \mathbf{I})^{-1} (\mathbf{H} - E_\alpha \mathbf{I}) = \mathbf{I}$ , we would have the result

$$(\mathbf{H} - E_\alpha \mathbf{I})^{-1} (\mathbf{H} - E_\alpha \mathbf{I}) \mathbf{c} = \mathbf{I} \mathbf{c} = \mathbf{c} = 0.$$

That is, each of the expansion coefficients, and so the approximation to the wave function  $\Psi_\alpha$ , *would vanish*! To prevent this, we need to *not* be able to find the inverse matrix,  $(\mathbf{H} - E_\alpha \mathbf{I})^{-1}$ .

It turns out that the inverse of a matrix is proportional to the inverse of its determinant. So, if we can arrange for the determinant of the matrix  $\mathbf{H} - E_\alpha \mathbf{I}$  to be equal to zero, then the inverse matrix will be infinite, and so effectively it will be undefined for the purposes of numerical computation.

The determinant,  $|\mathbf{H} - E_\alpha \mathbf{I}|$ , of the matrix  $\mathbf{H} - E_\alpha \mathbf{I}$  is

$$\begin{vmatrix} 12.38 - E_\alpha & -2.92 \\ 0.292 & 43.87 - E_\alpha \end{vmatrix} = (12.38 - E_\alpha) \times (43.87 - E_\alpha) - (-2.92) \times (-2.92)$$

This is a quadratic equation in the unknown energy,  $E_\alpha$ . Setting this quadratic equal to zero, we can solve for the two values of  $E_\alpha$  that satisfy the requirement that the matrix  $\mathbf{H} - E_\alpha \mathbf{I}$  *not* have an inverse.

16. Show that the two values of the energy are  $E_{\alpha=1} = 12.11$  and  $E_{\alpha=2} = 44.14$ .

What we have done is to find the two values of  $E_\alpha$  for which we will *not* be able to invert the matrix  $\mathbf{H} - E_\alpha \mathbf{I}$ , and so for which the values of the coefficients  $c_{1,\alpha}$  and  $c_{2,\alpha}$  will *not* vanish. The energies are found by solving  $|\mathbf{H} - E_\alpha \mathbf{I}| = 0$ . This is known as the *secular equation*. Finding the values of energy that solve the secular equation is how energy quantization arises in finding wave functions by expanding in a basis.

The exact value of the energy of the ground state of the distorted well is  $E_1 = 12.08$ , and that the first order approximation to the ground state energy is 12.38. The first, lowest energy that solves the secular equation, that is, the second order approximation to the energy of the ground state, is  $E_{\alpha=1} = 12.11$ , and so the second approximation to the energy is an improvement over the first order approximation to the energy, and now quite close to the exact energy, differing by only 0.03 diemsnsionless units (about 0.25 %).

## Part 2

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### ■ Solving the first order approximation to the wave function

At this point we know that

$$\begin{pmatrix} 12.38 - E_\alpha & -2.92 \\ -2.92 & 43.87 - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{pmatrix} = 0$$

has a non-trivial solution (that is, other than the expansion coefficients all being equal to zero) for two special values of the energy,  $E_\alpha$ .

|| 17. Show that the equations for  $\alpha = 1$  are

$$\begin{pmatrix} H_{1,1} - E_1 & H_{1,2} \\ H_{2,1} & H_{2,2} - E_1 \end{pmatrix} \begin{pmatrix} c_{1,1} \\ c_{2,1} \end{pmatrix} = \begin{pmatrix} 0.269 & -2.92 \\ -2.92 & 31.8 \end{pmatrix} \begin{pmatrix} c_{1,1} \\ c_{2,1} \end{pmatrix} = 0$$

|| and that the equations for  $\alpha = 2$  are

$$\begin{pmatrix} H_{1,1} - E_2 & H_{1,2} \\ H_{2,1} & H_{2,2} - E_2 \end{pmatrix} \begin{pmatrix} c_{1,2} \\ c_{2,2} \end{pmatrix} = \begin{pmatrix} -31.8 & -2.92 \\ -2.92 & -0.269 \end{pmatrix} \begin{pmatrix} c_{1,2} \\ c_{2,2} \end{pmatrix} = 0$$

The next step is to convert these two homogeneous algebraic equations into inhomogeneous equations. The way to do this is in two steps. The first step is to set one of the coefficients, say the first one, to the value one. The result is

$$\begin{pmatrix} H_{1,1} - E_{\alpha=1} & H_{1,2} \\ H_{2,1} & H_{2,2} - E_{\alpha=1} \end{pmatrix} \begin{pmatrix} 1 \\ (c')_{2,1} \end{pmatrix} = \begin{pmatrix} 0.269 & -2.92 \\ -2.92 & 31.8 \end{pmatrix} \begin{pmatrix} 1 \\ (c')_{2,1} \end{pmatrix} = 0$$

$$\begin{pmatrix} H_{1,1} - E_{\alpha=2} & H_{1,2} \\ H_{2,1} & H_{2,2} - E_{\alpha=2} \end{pmatrix} \begin{pmatrix} 1 \\ (c')_{2,2} \end{pmatrix} = \begin{pmatrix} -31.8 & -2.92 \\ -2.92 & -0.269 \end{pmatrix} \begin{pmatrix} 1 \\ (c')_{2,2} \end{pmatrix} = 0$$

This amounts to solving for the ratio of the two coefficients, and we indicate this by putting a prime on the other coefficient of each pair. We can later fix the absolute value of the two coefficients from each set of equations by requiring that the resulting wave functions be normalized.

The second step is to ignore the first equation of each set. The remaining equations

$$(H_{2,2} - E_{\alpha=1}) (c')_{2,1} = -H_{2,1}$$

$$(H_{2,2} - E_{\alpha=2}) (c')_{2,2} = -H_{2,1}$$

allow us to solve for the remaining coefficients,

$$(c')_{2,1} = -(H_{2,2} - E_{\alpha=1})^{-1} H_{2,1}$$

$$(c')_{2,2} = -(H_{2,2} - E_{\alpha=2})^{-1} H_{2,1}.$$

18. Evaluate the coefficients  $(c')_{2,1}$  and  $(c')_{2,2}$ . Answer: 0.0919 and -10.9.

19. Show that the normalization constant of the first order approximation to the wave function is  $1/\sqrt{1 + (c')_{2,\alpha}^2}$ .

20. Show that the normalized approximate wave functions are

$$\Psi_1 \approx \Psi_{1,\text{approx}}(x) = 1.41 \sin(\pi x) + 0.129 \sin(2\pi x),$$

$$\Psi_2 \approx \Psi_{2,\text{approx}}(x) = 0.129 \sin(\pi x) - 1.41 \sin(2\pi x).$$

Here is a comparison of the approximate wave function to the exact wave function of the distorted well and to the wave function of the undistorted well.

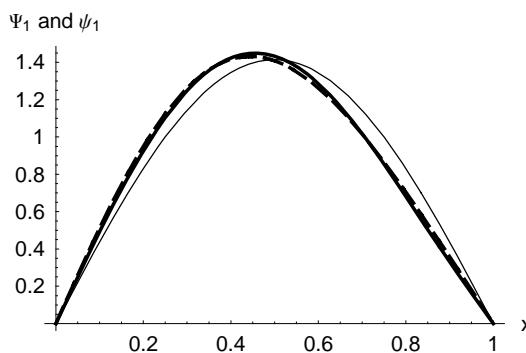


Figure 7. Exact ground state wave function,  $\Psi_1(x)$  (thick curve), of the distorted well, with potential energy  $(2x)^5$ , approximation to the exact wave function,  $\Psi_{1,\text{approx}}(x)$  (thick, dashed curve), and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$  (thin curve), of the undistorted well.

21. What do you conclude from the plot?

## ■ The other approximate energy and wave function.

We determined *two* values of the energy such that the secular determinant vanishes. The second energy is an approximation to the first excited state of the distorted well.

22. Show that the zero order approximation to the energy of the first excited state is 39.48.

23. Show that the first order approximation to the energy of the first excited state,

$$E_2 \approx \epsilon_2 + \int_0^1 \psi_2(x)^* (H - H^{(0)}) \psi_2(x) dx,$$

gives the value  $E_2 \approx 43.87$ .

The exact value of the energy of the first excited state of the distorted well is  $E_2 = 43.77$ , and so once again, the first order approximation to the energy, 43.87, is quite good. The second energy that solves the secular equation, that is, the second order approximation to the energy of the first excited state, is  $E_{\alpha=2} = 44.14$ . Since  $E_{\alpha=2}$  is not as close to the exact energy as the first order approximation, in this case the first order approximation to the energy is doing a slightly better job than the second order approximation to the energy.

Here is a comparison of the normalized approximate wave function,  $\Psi_{2,\text{approx}}$ , to the exact wave function of the distorted well and to the wave function of the undistorted well, for the first excited state.

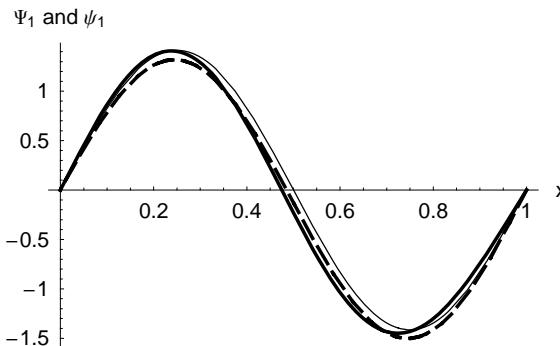


Figure 8. Exact first excited state wave function,  $\Psi_2(x)$  (thick curve), of the distorted well, with potential energy  $(2x)^5$ , approximation to the exact wave function,  $\Psi_{2,\text{approx}}(x)$ , (thick, dashed curve), and the wave function,  $\psi_2(x) = \sqrt{2} \sin(2\pi x)$  (thin curve), of the undistorted well. The exact and approximate wave functions have been multiplied by  $-1$  to match the phase of the wave function of the undistorted well.

24. What do you conclude from the plot?

## ■ Accuracy of the second order approximation to energy and the first order approximation to the wave function

Let's see how the second order approximation works for a modified version of the distorted well.

29. Show that the equations for the expansion coefficients are now

$$\begin{pmatrix} H_{1,1} - E_\alpha & H_{1,2} \\ H_{2,1} & H_{2,2} - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{pmatrix} = \begin{pmatrix} 90.27 - E_\alpha & -93.45 \\ -93.45 & 180.2 - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{pmatrix} = 0$$

The values of  $E_\alpha$  that solve the secular equation corresponding to these equations are  $E_{\alpha=1} = 31.52$  and  $E_{\alpha=2} = 238.9$ . As before, the lower of these two values is the second order approximation to the ground state energy.

Proceeding in the same way as before, you can find that the expansion coefficients, relative to  $c_{1,\alpha} = 1$ , are  $(c')_{2,1} = 0.629$  and  $(c')_{2,2} = -1.591$ , and so that the normalized approximation to the ground state wave function is  $\Psi_1 \approx 1.20 \sin(\pi x) + 0.753 \sin(2\pi x)$ .

Here is a comparison of the normalized approximate wave function to the exact wave function of the new distorted well and to the wave function of the undistorted well.

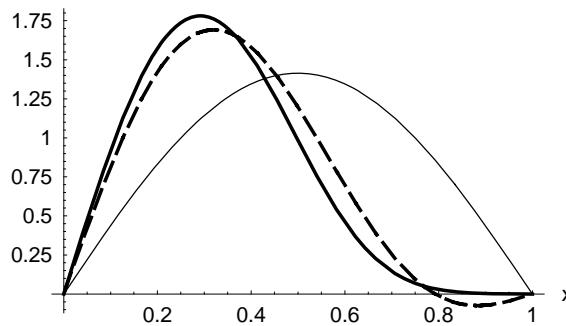


Figure 9. Exact ground state wave function,  $\Psi_1(x)$  (thick curve), of the modified distorted well, with potential energy  $(4x)^5$ , approximation to the exact wave function (thick, dashed curve), and the wave function,  $\psi_1(x) = \sqrt{2} \sin(\pi x)$ , (thin curve) of the undistorted well.

25. What do you conclude from the plot?

Recall that the exact value of the energy of the ground state of the modified distorted well is  $E_1 = 29.62$ , and that the first order approximation to the ground state energy is 90.27; that is, the first order approximation to the energy was very poor for this case. The first, lowest energy that solves the secular equation, that is, the second order approximation to the energy of the ground state, is  $E_{a=1} = 31.52$ , and so the second order approximation to the energy is quite good, and a major improvement over the first order approximation to the energy.

Here is a table consisting of (1) the ground state energy of the undistorted well, the first order and second order approximations to the energy of the distorted well, and the exact energy of the distorted well, and (2) the ground state energy of the undistorted well, the first order and second order approximations to the energy of the modified distorted wells, and the exact energy of the modified distorted well.

	zero order	first order	second order	exact
$(2x)^5$ distortion	9.86879	12.3812	12.1127	12.0814
$(4x)^5$ distortion	9.86879	90.2657	31.5234	29.6288

Approximate and exact energies for the alternative distorted wells. The distortion is the deviation  $H - H^{(0)}$  from the infinite square well.

26. Why do you suppose in this case, for the modified version of the distorted well, with potential energy  $(4x)^5$ , the first order approximation is so poor whereas the first order approximation was so good for the original version of the distorted well, with potential energy  $(2x)^5$ .

27. Based the table, and the analyses of the wave function of the undistorted well, and the first order approximate wave functions and exact wave functions of the distorted wells, shown in figures 7 and 9, propose guidelines on how to best approximate energies and wave functions in terms of those of a reference system.

## ■ The approximate wave functions "diagonalize" the hamiltonian (optional)

This last part explores some general properties of the procedure used to find the second order energies and the corresponding first order wave functions, for the example of the well with distortion  $(2x)^5$ . You may omit this part if you are pressed for time, leaving it for study outside of workshop.

28. Make use of the orthonormality of the basis functions,  $\psi_1$  and  $\psi_2$ , to show that  $\int_0^1 \Psi_{2,\text{approx}}(x) \Psi_{1,\text{approx}}(x) dx = 0$ .

29. Show that the matrix of the hamiltonian of the distorted well in the basis of its approximate wave functions,  $\Psi_{1,\text{approx}}$  and  $\Psi_{2,\text{approx}}$ , is a diagonal matrix, and that the elements on the diagonal are the second order approximations to the energy.

The last question illustrates the general result that solving the Schrödinger equation by expansion in a basis is equivalent to finding the combinations of basis functions in terms of which the matrix of the hamiltonian is diagonal. It is for this reason that solution to the Schrödinger equation is often referred to as *diagonalizing the hamiltonian*.

Formally, the process of diagonalization is carried out by a particular kind of matrix multiplication known as a *similarity transformation*. A similarity transformation of a matrix  $\mathbf{H}$  by a matrix  $\mathbf{U}$  is defined as the matrix product  $\mathbf{U}^{-1} \mathbf{H} \mathbf{U}$ . In this case,  $\mathbf{U}$  is the matrix whose first row is the expansion coefficients  $c_{j,\alpha=1}$  and whose second row is the expansion coefficients  $c_{j,\alpha=2}$ ,

$$\mathbf{U} = \begin{pmatrix} c_{1,1} & c_{2,1} \\ c_{1,2} & c_{2,2} \end{pmatrix} = \begin{pmatrix} 0.996 & 0.0915 \\ 0.0915 & -0.996 \end{pmatrix}$$

The matrix  $\mathbf{U}$  has the special property that its transpose,  $\tilde{\mathbf{U}}$ , is its inverse. This property is called orthogonality.

30. Demonstrate that  $\mathbf{U}$  is an orthogonal matrix, by showing that  $\tilde{\mathbf{U}} \mathbf{U} = \mathbf{I}$ .

31. Show that  $\mathbf{U}$  diagonalizes the hamiltonian matrix,

$$\mathbf{H} = \begin{pmatrix} 12.4 & -2.92 \\ -2.92 & 43.9 \end{pmatrix}.$$

That is, show that

$$\mathbf{U}^{-1} \mathbf{H} \mathbf{U} = \begin{pmatrix} E_{\alpha=1} & 0 \\ 0 & E_{\alpha=2} \end{pmatrix}.$$