Schrödinger Program Assignment

Program and assignment designed by:

Matthew N. Srnec
Franciscan University of Steubenville
Department of Chemistry, Physics, and Engineering
Sts. Cosmas and Damian Hall 215

Shiv Upadhyay, and Dr. Jeffry D. Madura
Duquesne University
Department of Chemistry and Biochemistry
Center for Computational Sciences
Madura Research Group
Mellon Hall 320

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This assignment serves to reinforce several concepts discussed in undergraduate physical chemistry. Such examples include: particle in an infinite well, particle in a finite well, particle in a double finite well of equal depth, particle in a double finite well of unequal depth, particle in a harmonic well, particle in Morse potential energy well, and particle in a Kronig-Penney potential. Moreover, this assignment also provides experience working with the Python programming language and a numerical method for solving Schrödinger's equation. For background information, methods employed, and instructions for getting started, please see the corresponding manuscript and supporting information. This assignment is suitable as an individual or group project. A single write-up should be submitted that summarizes the Schrödinger program(1-2 paragraphs), answers the questions outlined in each case (include figures where directed), and discusses (1-2 paragraphs) how these examples can be related back to chemical systems that we encounter in chemistry.

Cases and Questions

Each of the following sections briefly describes a case of the Schrodinger.py program, outlines the variables to modify, presents a sample plot, and lists several questions to be answered. In *ALL* cases, the following questions should also be answered *ALONG WITH* the specific questions for each case:

1. What happens to the energy levels as the width of the potential energy well, W, increases/decreases?

2. What happens to the spacing between wavefunctions with increasing energy?

3. What is the general rule for the number of nodes of a wavefunction? Does what you observe agree with the general rule?

Case 1. *Particle in an Infinite Potential Energy Well*

The first case to investigate is the particle in an infinite potential energy well. Here, the width of the potential energy well (W) and the number of wavefunctions for plotting can be modified. $\hbar$ and m are both set to 1 in all calculations so that energies are calculated in atomic units (a.u.). Upon calculating the eigenvectors (wavefunctions) and the eigenvalues (energies), the results are plotted. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are W = 5 a.u. and number of wavefunctions = 7.

Users should compare the energies calculated to the exact energies predicted by:

$$E = \frac{n^2 h^2}{8mW^2},$$

where n is the energy level, h is Planck's constant, m is the mass of an electron, W is the *total width* of the well, $\hbar$ and m are 1, and $h = 2\pi$. For n = 1, the predicted energy (in atomic units) is

$$E = \frac{1^2 \cdot (2\pi)^2}{8 \cdot 5^2} = 0.0987 \text{ a.u.}$$

How well do the calculated energy values from the program compare to the energies for a particle-in-a-box discussed above? Compare these energy values for various values of n.

In addition to the general questions described previously, students should answer the following questions in their write-up for case 1:

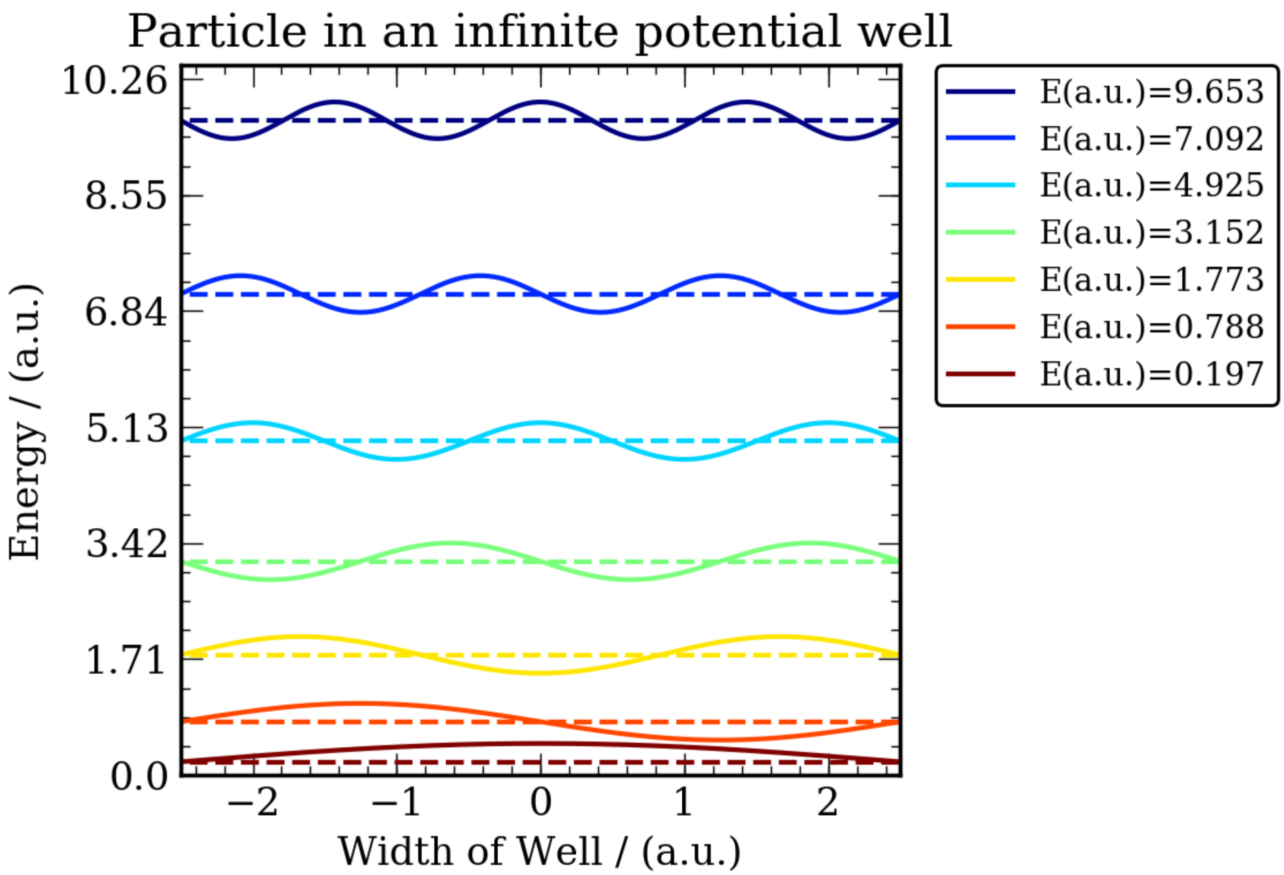
1. Briefly summarize Case 1 of the Schrodinger.py program. Comment specifically on the modifiable input variables.

2. When W = 3 a.u., what is the energy value of the 7th bound wavefunction? Include a plot of your results.

3. Comment on the accuracy of the 3-point finite-difference method in approximating the energy calculated above.

4. Try 2 additional sets of inputs for Case 1 and include the plots in your write-up. Be sure to explain what variable(s) was/were changed and the significance they had on the results.

5. For the 2 additional sets of inputs, also include a plot of the probability density for each. Provide an explanation of how this probability density differs from the plots in question #4 above.



Case 2. *Particle in a Finite Potential Energy Well*

In addition to the width of the potential energy well (W), the depth (D) of the well can be modified in this case. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: W = 1 a.u. and D = 100 a.u.

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 2:

1. Briefly explain the differences between Cases 1 and 2. In particular, comment on the definition of zero energy in these two cases. Why is there such a significant difference? Is the zero energy at the top or bottom of the infinite well in Case 1? Likewise, is the zero energy at the top or bottom of the finite well in Case 2?

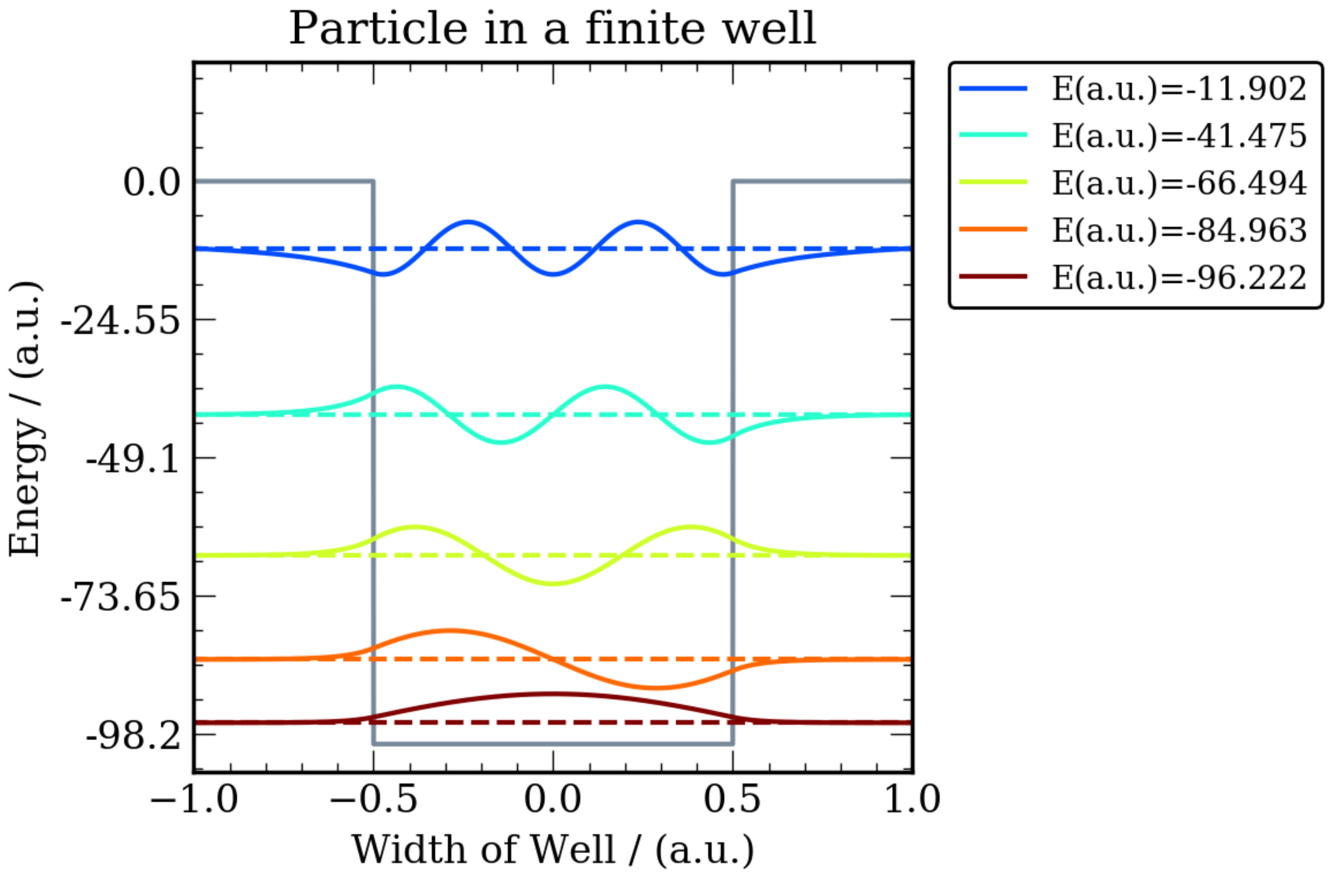
2. How many bound energy levels are capable of existing in the finite potential energy well if W = 5 a.u. and D = 400 a.u.? Include a plot of your results.

3. Are the wavefunctions permitted to exist outside the finite potential energy well barriers? If so, what is this phenomenon called? Provide a brief description of the phenomenon.

4. When W = 3 a.u. and D = 52 a.u., what is the energy of the 5th bound wavefunction? Include a plot of your results.

5. Try two additional sets of inputs for Case 2 and include the plots in your write-up. Be sure to explain what variable(s) was/were changed and the significance they had on the results.

6. For the 2 additional sets of inputs, also include a plot of the probability density for each. Provide an explanation of how this probability density differs from the plots in question #5 above.


Particle in a finite well
E(a.u.)=-11.902
E(a.u.)=-41.475
E(a.u.)=-66.494
E(a.u.)=-84.963
E(a.u.)=-96.222
Energy / (a.u.)
0.0
-24.55
-49.1
-73.65
-98.2
−1.0
−0.5
0.0
0.5
1.0
Width of Well / (a.u.)

Case 3. *Particle in a Double Finite Potential Energy Well of Equal Width and Depth*
In addition to the width (W) and depth (D) of the finite potential energy well, users can also vary the distance (B) between wells in this case. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: W = 1 a.u., D = 50 a.u., and B = 2 a.u..

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 3:

1. Briefly explain the differences between Case 3 and Cases 1 and 2.

2. How many bound energy levels are capable of existing in the finite potential energy well if W = 4 a.u., B = 2 a.u., and D = 80 a.u.? Include a plot of your results.

3. Does the phenomenon discussed in Case 2 likewise exist in Case 3?

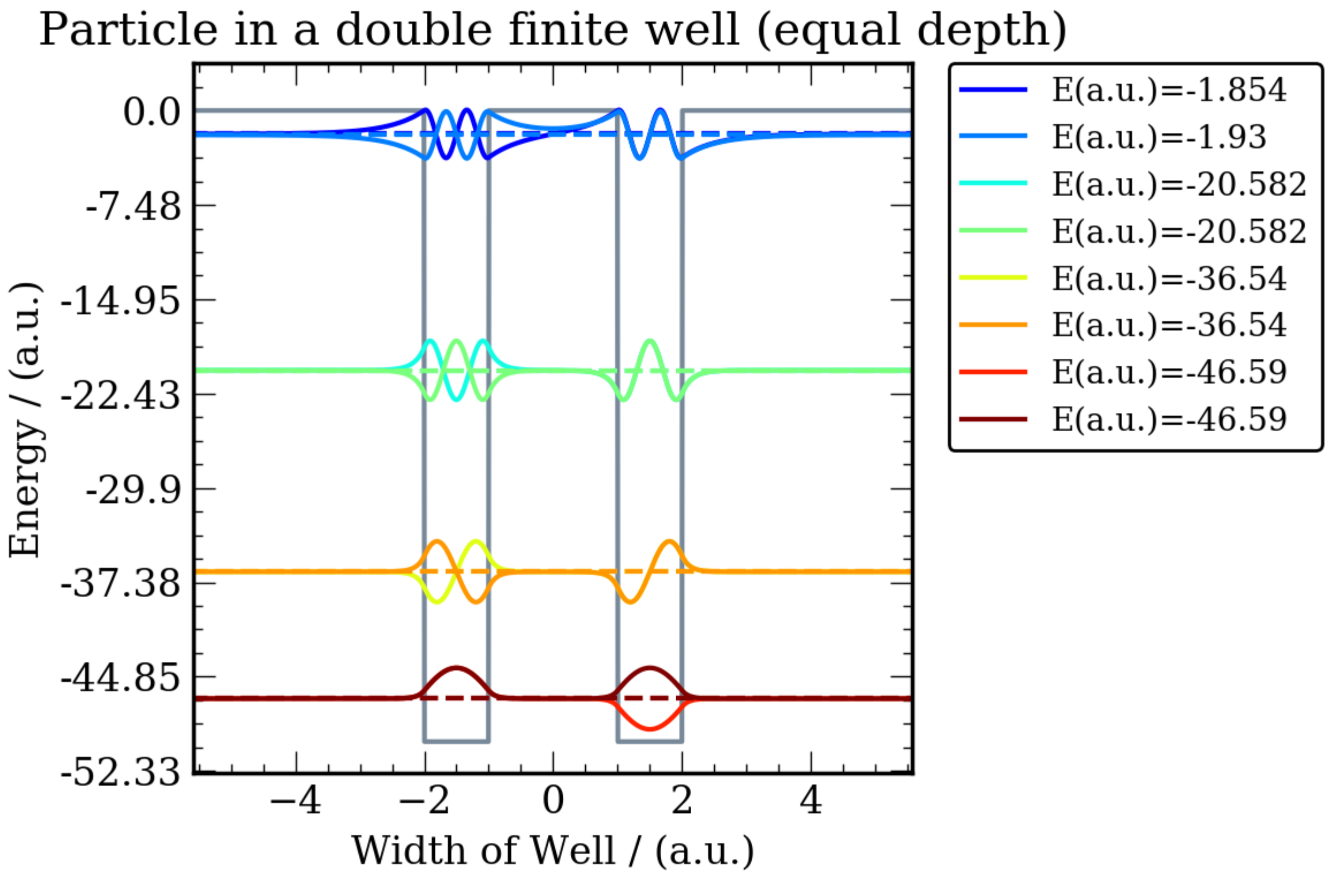
4. When W = 3 a.u., B = 4 a.u., and D = 150 a.u., what is the energy of the 6th bound wavefunction? Include a plot of your results.

5. What do you observe as W, B, and D are changed individually?

6. Considering the inputs in question 2 of this case, what unique feature do you notice about the wavefunctions? In quantum mechanics, what term is given to this phenomenon?

7. Choose a width (W) and depth (D) of the finite potential energy wells. Incrementally decrease the distance between the wells from the maximum allowed value to the minimum allowed value. What do you notice about the wavefunction behavior as the wells are brought to the minimum separation distance? Discuss what is occurring in the context of a chemical system.

8. Provide an example of a chemical system that this case represents. Do you think that the square potentials depicted in the plots are an accurate representation of atomic potentials in molecules? How would you expect the potential energy wells of these atoms to be different than the step potentials used in the Schrodinger.py program?


Particle in a double finite well (equal depth)
Energy / (a.u.)
0.0
-7.48
-14.95
-22.43
-29.9
-37.38
-44.85
-52.33
−4
−2
0
2
4
Width of Well / (a.u.)
E(a.u.)=-1.854
E(a.u.)=-1.93
E(a.u.)=-20.582
E(a.u.)=-20.582
E(a.u.)=-36.54
E(a.u.)=-36.54
E(a.u.)=-46.59
E(a.u.)=-46.59

Case 4. *Particle in a Double Finite Potential Energy Well of Unequal Depth and Width*
In this case, students can enter unequal widths (W1 and W2) and depths (D1 and D2) of their wells. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: W1 = 0.5 a.u., W2 = 1.0 a.u., B = 0.8 a.u., D1 = 30 a.u., and D2 = 75 a.u.

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 4:

1. Briefly explain the differences between Case 4 and Cases 1,2, and 3.

2. How many bound energy levels are capable of existing in the finite potential energy well if W1 = 2 a.u., W2 = 4 a.u., B = 2 Å, D1 = 50 a.u., and D2 = 150 a.u.? Include a plot of your results.

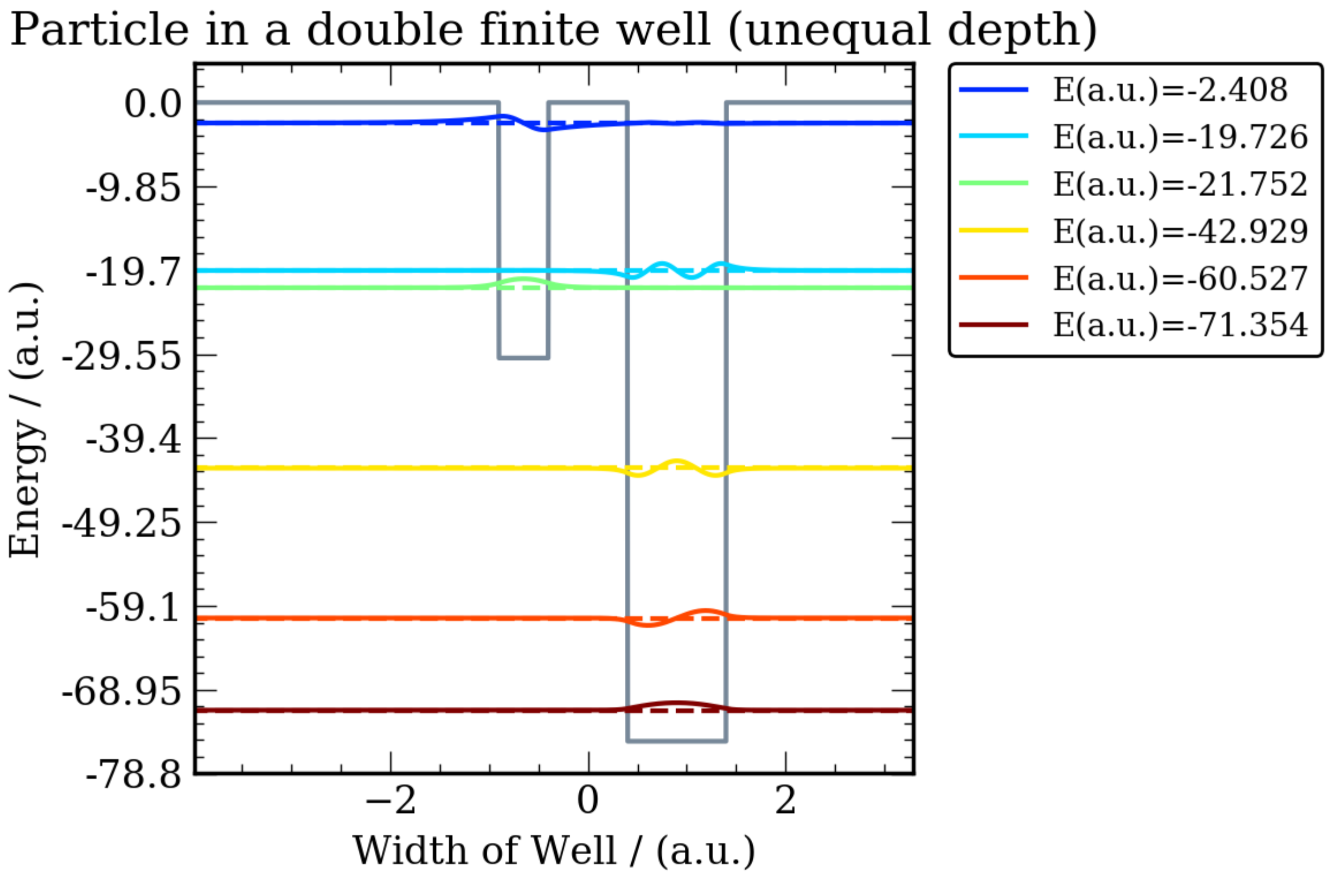
3. Does the phenomenon discussed in cases 2 and 3 likewise exist in case 4?

4. When W1 = 0.8 a.u., W2 = 1.3 a.u., B = 4 a.u., D1 = 30 a.u., and D2 = 65 a.u., what is the energy of the 4th bound wavefunction? Include a plot of your results.

5. What do you observe as W1, W2, B, D1, and D2 are changed individually?

6. Choose a width (W) and depth (D) of the finite potential energy wells. Incrementally decrease the distance between the wells from the maximum allowed value to the minimum allowed value. What do you notice about the wavefunction behavior as the wells are brought to the minimum separation distance? Discuss what is occurring in the context of a chemical system.

7. In the context of chemical systems, how does Case 4 differ from Case 3?



Particle in a double finite well (unequal depth)
0.0
-9.85
-19.7
-29.55
-39.4
-49.25
-59.1
-68.95
-78.8
Energy / (a.u.)
−2
0
2
Width of Well / (a.u.)
E(a.u.)=-2.408
E(a.u.)=-19.726
E(a.u.)=-21.752
E(a.u.)=-42.929
E(a.u.)=-60.527
E(a.u.)=-71.354

Case 5. *Particle in a Harmonic Potential Energy Well*

The force constant and the depth (D) of the well can be modified in this case. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: force constant = 0.5 and D = 4 a.u.

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 5:

1. Briefly explain how this case differs from the previous cases.

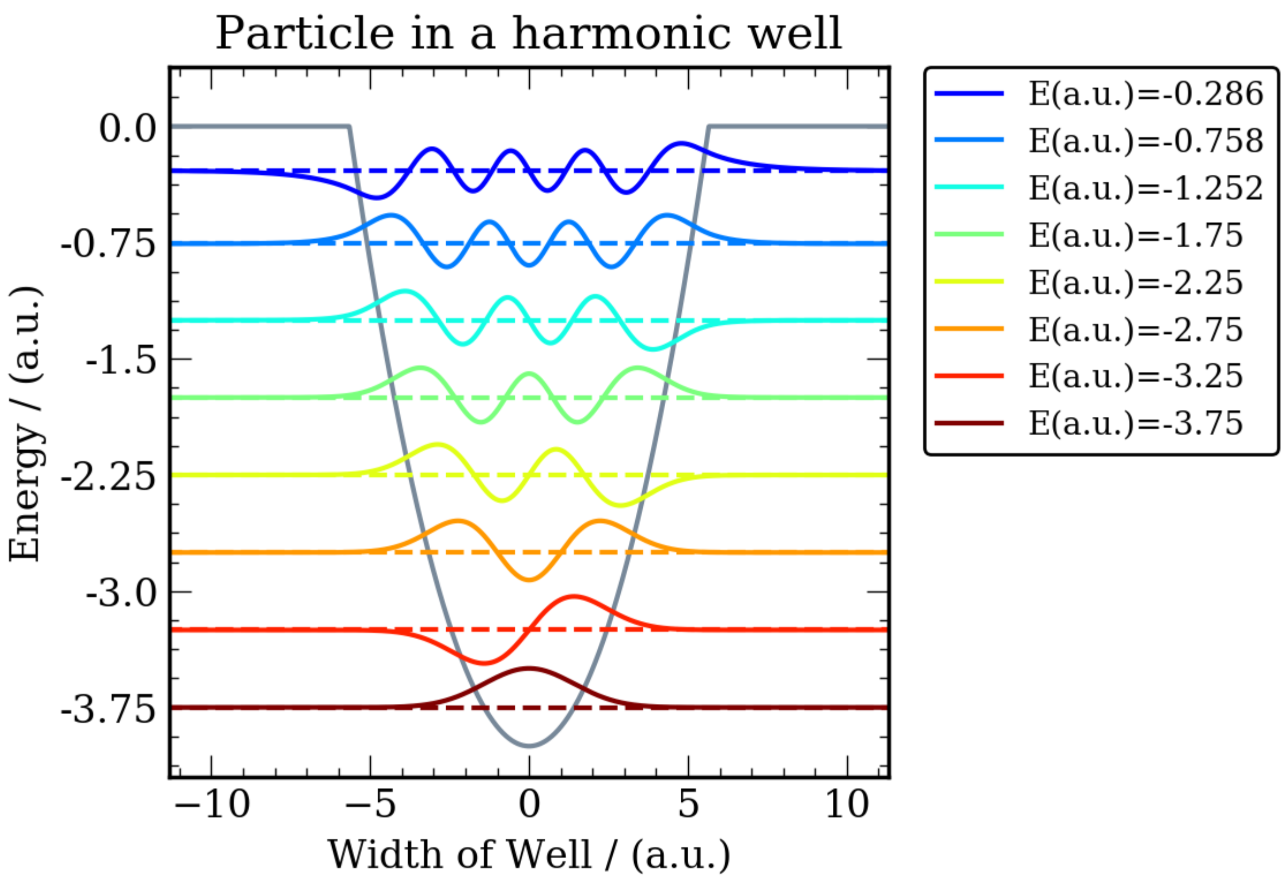
2. How many bound energy levels are capable of existing in the finite potential energy well if force constant = 0.6 and D = 10 a.u.? Include a plot of your results.

3. Are the wavefunctions permitted to exist outside the harmonic potential energy well? If so, what is this phenomenon called? Provide a brief description of the phenomenon.

4. When W = 0.8 a.u. and D = 6 a.u., what is the energy of the 5th bound wavefunction? Include a plot of your results.

5. Try two additional sets of inputs for case 5 and include the plots in your write-up. Be sure to explain what variable(s) was/were changed and the significance they had on the results.

6. For the 2 additional sets of inputs, also include a plot of the probability density for each. Provide an explanation of how this probability density differs from the plots in question #5 above.



Particle in a harmonic well
E(a.u.)=-0.286
E(a.u.)=-0.758
E(a.u.)=-1.252
E(a.u.)=-1.75
E(a.u.)=-2.25
E(a.u.)=-2.75
E(a.u.)=-3.25
E(a.u.)=-3.75
0.0
-0.75
-1.5
-2.25
-3.0
-3.75
Energy / (a.u.)
−10
−5
0
5
10
Width of Well / (a.u.)

Case 6. *Particle in a Morse Potential Energy Well*

The force constant and the depth (D) of the well can be modified in this case. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: force constant = 0.3 and D = 2 a.u.

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 6:

1. Briefly explain how this case differs from the previous cases.

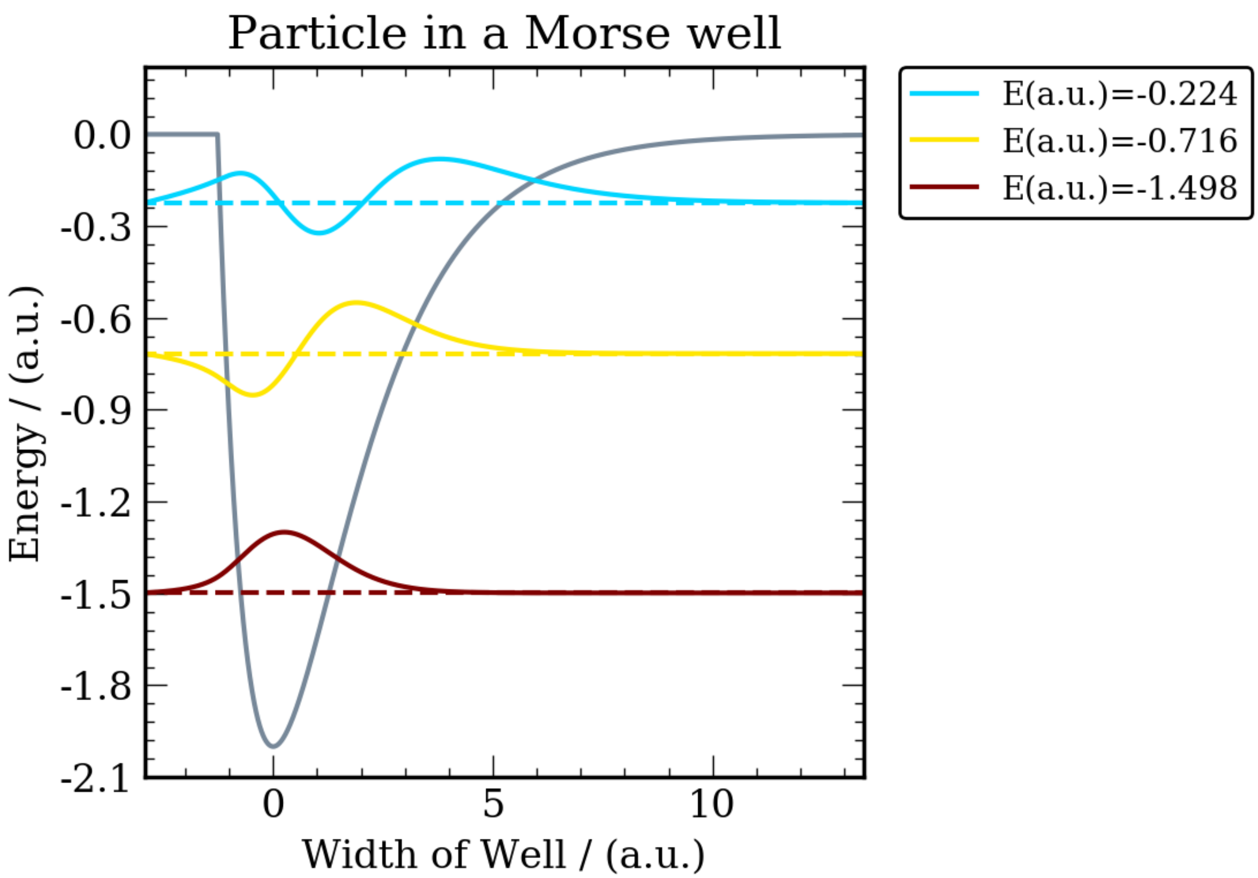
2. How many bound energy levels are capable of existing in the finite potential energy well if force constant = 0.4 and D = 4 a.u.? Include a plot of your results.

3. Are the wavefunctions permitted to exist outside the finite potential energy well barriers? If so, what is this phenomenon called? Provide a brief description of the phenomenon.

4. When force constant = 0.7 and D = 5 a.u., what is the energy of the 5th bound wavefunction? Include a plot of your results.

5. Try two additional sets of inputs for case 6 and include the plots in your write-up. Be sure to explain what variable(s) was/were changed and the significance they had on the results.

6. For the 2 additional sets of inputs, also include a plot of the probability density for each. Provide an explanation of how this probability density differs from the plots in question #5 above.



Particle in a Morse well
E(a.u.)=-0.224
E(a.u.)=-0.716
E(a.u.)=-1.498
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
Energy / (a.u.)
0
5
10
Width of Well / (a.u.)

Case 7. *Kronig-Penney Finite Well*

The width (W) and depth (D) of repeating finite wells, the distance between finite wells (B) and the number of repeating wells (n) can be modified in this case. An example plot of the wavefunctions and energies for this case is provided on the following page. The input parameters are: W = 1.0 a.u., D = 30 a.u., B = 1.0 a.u., and n = 5.

In addition to the general questions described previously, students should answer the following questions in their write-up for Case 7:

1. Briefly explain how this case differs from the previous cases. Hint: Consider the boundary conditions.

2. How many bound energy levels are capable of existing in the finite potential energy wells if W = 2 a.u., D = 50 a.u., and B = 1 a.u.? Include a plot of your results.

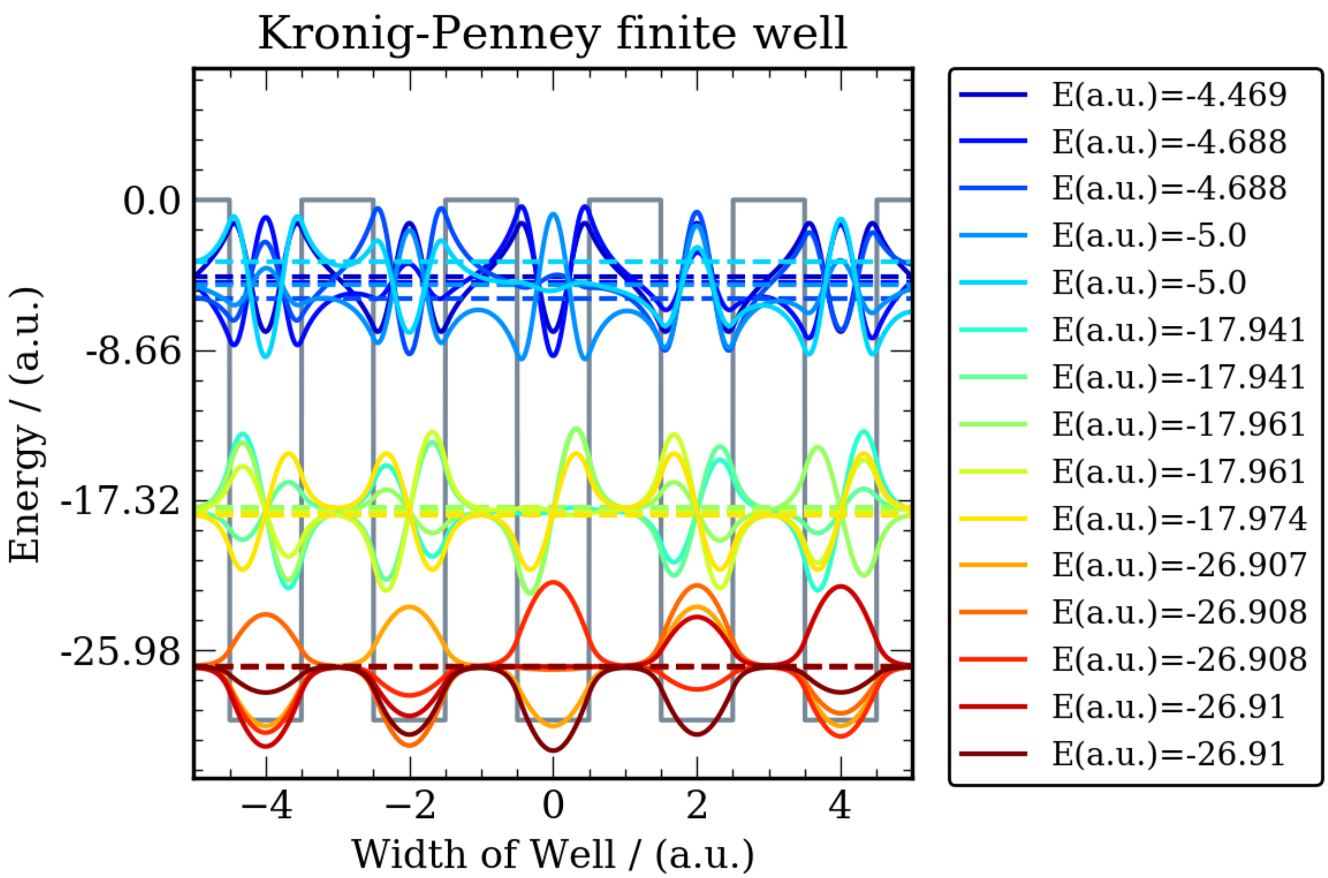
3. Are the wavefunctions permitted to exist outside the finite potential energy well barriers? If so, what is this phenomenon called? Provide a brief description of the phenomenon.

4. When W = 1 a.u., D = 80 a.u., and B = 1 a.u. what is the energy of the 5th bound wavefunction? Include a plot of your results.

5. Try two additional sets of inputs for case 7 and include the plots in your write-up. Be sure to explain what variable(s) was/were changed and the significance they had on the results.

6. For the 2 additional sets of inputs, also include a plot of the probability density for each. Provide an explanation of how this probability density differs from the plots in question #5 above.

7. Finite size effects arise when treating periodic systems because treating a few wells periodically is different than treating an infinite number of wells. How does the energy of the ground state change as more periodic wells are included?


Kronig-Penney finite well
0.0
-8.66
-17.32
-25.98
Energy / (a.u.)
−4
−2
0
2
4
Width of Well / (a.u.)
E(a.u.)=-4.469
E(a.u.)=-4.688
E(a.u.)=-4.688
E(a.u.)=-5.0
E(a.u.)=-5.0
E(a.u.)=-17.941
E(a.u.)=-17.941
E(a.u.)=-17.961
E(a.u.)=-17.961
E(a.u.)=-17.974
E(a.u.)=-26.907
E(a.u.)=-26.908
E(a.u.)=-26.908
E(a.u.)=-26.91
E(a.u.)=-26.91