CHEM 361B - Lecture 14 Activity

Approximative Methods

1. To illustrate the variational method, we will solve the particle in an infinite square potential using the variational method. Our trial wavefunction will have the form:

$$\phi(x) = c_1 f_1 + c_2 f_2$$

where

$$f_1 = x(1-x) \quad \text{and} \quad f_2 = x^2(1-x)^2$$

For convenience, we will set the length of the box, $a = 1$.

(a) Verify that the trial wavefunction satisfies the boundary conditions for the particle in a infinite square potential.

(b) Variational Principle Step 1

i. Show that

$$\begin{aligned}\int_0^1 \phi^* \hat{H} \phi dx =& c_1^2 \int_0^1 f_1^* \hat{H} f_1 dx + c_1 c_2 \int_0^1 f_1^* \hat{H} f_2 dx + c_1 c_2 \int_0^1 f_2^* \hat{H} f_1 dx + c_2^2 \int_0^1 f_2^* \hat{H} f_2 dx \\ =& c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}\end{aligned}$$

ii. Evaluate the four integrals and show that

$$H_{11} = \frac{\hbar^2}{6m}; \quad H_{12} = H_{21} = \frac{\hbar^2}{30m}; \quad H_{22} = \frac{\hbar^2}{105m}$$

Feel free to use Wolframalpha to do this. For example, you can find H_{12} by applying the second derivative to a function using

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second derivative x^2(1-x)^2
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which will give $x(12x-12)+2$. You can then integrate between 0 and 1 using

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int x(1-x) (-h^2/(2m)) (x (12 x - 12) + 2), x=0..1
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(c) Variational Principle Step 2

i. Show that

$$\begin{aligned}\int_0^1 \phi^* \phi dx =& c_1^2 \int_0^1 f_1^* f_1 dx + c_1 c_2 \int_0^1 f_1^* f_2 dx + c_1 c_2 \int_0^1 f_2^* f_1 dx + c_2^2 \int_0^1 f_2^* f_2 dx \\ =& c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}\end{aligned}$$

ii. Evaluate the four integrals and show that

$$S_{11} = \frac{1}{30}; \quad S_{12} = S_{21} = \frac{1}{140}; \quad S_{22} = \frac{1}{630}$$

Feel free to use Wolframalpha to do this.

(d) Variational Principle Step 3. Show that

$$E_\phi = \frac{c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}}{c_1^2 S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}$$

(e) Variational Principle Step 4

i. Take E_ϕ and multiply both sides of the expression by $c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}$ to get

$$(c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22})E_\phi = c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}$$

ii. Take the derivative of this expression with respect to c_1 and set $dE_\phi/dc_1 = 0$ to get

$$0 = c_1(H_{11} - S_{11}E_\phi) + c_2(H_{12} - S_{12}E_\phi) \tag{1}$$

iii. Take the derivative of this expression with respect to c_2 and set $dE_\phi/dc_2 = 0$ to get

$$0 = c_1(H_{12} - S_{12}E_\phi) + c_2(H_{22} - S_{22}E_\phi) \tag{2}$$

(f) Variational Principle Step 5

i. Express Equations 1 and 2, as the following secular determinant

$$\begin{vmatrix} H_{11} - S_{11}E_\phi & H_{12} - S_{12}E_\phi \\ H_{12} - S_{12}E_\phi & H_{22} - S_{22}E_\phi \end{vmatrix} = 0$$

ii. Evaluate the secular determinant using WolframAlpha:

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determinant{{h^2/(6m)-x/30,h^2/(30m)-x/140},
{h^2/(30m)-x/140,h^2/(105m)-x/630}}=0
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and show that there are two roots for $E_{\phi,min}$:

$$E_{\phi,min} = 4.93487\frac{\hbar^2}{m} \quad \text{and} \quad 51.065\frac{\hbar^2}{m}$$

(g) Compare the smaller of the two solutions to the actual ground state solution to the particle in a box. Why would we choose the smaller of the two solutions? Is the smaller solution still larger than the actual solution?

(h) The constants c_1 and c_2 can be solved for leading to a complete solution for ϕ:

$$\phi(x) = 4.40378f_1 + 4.99133f_2$$

Plot this expression as well as the exact ground state wavefunction solution for the particle in an infinite square potential in WolframAlpha by typing:

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plot 4.40378x(1-x)+4.99133x^2(1-x)^2, sqrt(2)sin(pi*x), x=0..1
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Compare the two lines.