**Guided Practice in Quantum Approximation #1 : Chemistry 6854**

**Physical Chemistry Alfred State College**

**Solving a Variational Problem Using a Trial Function φ with an Adjustable Constant**

Assume: L=1 in the ground state for a simplified particle in a box where we have picked a unit system such that π=m= ħ=1. In this case, the quantum Hamiltonian for the particle in the box is:

1. Given that E(n)= **π2** ħ 2n2/2mL2 is the exact energy for the system, what is E at n=1 in our assumed unit system ? Eo(exact, n=1) = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Let’s try a trial function of the form: φ(x) = ax3 + x2 +cx

1. Is it continuous and differentiable from 0🡪1? YES NO
2. Can we find a relationship between a and c so that φ(0)=φ(1)=0 ? YES NO
3. If yes to (c) express **c** as function of **a**:

**c =**

1. Now we can use Maple, and substitute in the relationship above for **c**, to compute the relevant energy estimate for the critical variational expression:

**Eφ= <φ\*||φ>**

 **<φ|φ>**

How to do it: (answers to each step are in appendix)

Step 1: plug c as function of a into the trial function:

φ(x) = ax3 + x2 +cx =

Step 2: Use Maple or compute φ = -

φ = - =

(This is the energy operator acting on the trial function

Step 3: Use Maple to express the product φ\*||φ: =- ½ φ(x) . . You can save the expression in Maple or write it down in the box below:

Step 4: Use Maple to integrate φ\*||φ from 0🡪1=L. This is <φ\*||φ >. You don’t have to write this (ugly) function down but check answers in appendix below )

 1

Step 5: compute the normalization integral <φ\*|φ> = ∫φ2dx using Maple.

 0

Step 6: divide <φ\*||φ >/<φ\*|φ> = Eφ (it’s big and ugly)

Step 7: in Maple take the derivative of the above by clicking on the d/dx button, and putting the expression above in parentheses within the derivative, then hit return. (Now it’s bigger and uglier)

Step 8: Now copy the whole expression from step. Copy it to a fresh line and set it = and return.

Select this expression, right click and `solve for a variable (**a**)’ which is the goal of a variational minimization problem. If you do this right, two choices for **a** appear for the the solutions to

Write down each **a** value from step 8

**a1=\_\_\_\_\_\_\_\_\_\_ a2= \_\_\_\_\_\_**

1. Computing Eφ

To see what the estimated energies are for either choice of **a,**

 plug each one back into the original expression below, using Maple by selecting the

integrated expression from **step 6** , right clicking and selecting `evaluate at a point’. Plug in a1 and a2

**Eφ= <φ\*||φ> \_\_\_\_\_ \_\_\_\_\_\_**

 **<φ|φ> E(a1) E(a2)**

1. Given your answers aboveand the actual value for E0 decide whether our assumed φ sucks or not **SUCKS NOT SUCKS**
2. Do our solutions at least obey the variational principle ??? Why or why not ???

Appendix

Step 1: φ(x) = ax3 + x2 –(1+a)x

Step 2: φ = - ½ (6ax +2)

 Step 3: φ φ =-φ(x) . - ½ 

Step 4: <φ\*||φ > = 

Step 5: <φ|φ>=

Step 6:Eφ= <φ|φ>/<φ|φ> = 

Step 7: dEφ/da= 

Step 8: a1=0, a2=-2/3

f)Computing Eφ

**Eφ= <φ\*||φ> \_\_\_\_5\_\_\_\_ \_\_\_\_21\_\_\_\_\_\_\_\_**

 **<φ|φ> a1(=0) a2(=-2/3)**