**Guided Practice in Quantum Approximation #2 : Chemistry 6854**

**Physical Chemistry Alfred State College**

**Solving a Variational Problem with an Assumed Trial Function φ = c1φ1 +c2φ2**

*In this guided practice example, we try out the other variational strategy which is to pick several `fixed’ form trial wave functions, φ1 and φ2 and then apply the `secular’ determinant described in* ***Supplement 8*** *to minimize Eφ vs c1, and c2. The reason you were `forced’ to review determinants was essentially because it forms the basis of this variational strategy. As noted earlier in* ***Supplement 8****, the approach is the heart of modern chemical methods to model molecular systems. The approach is referred to as `Generalized Molecular Orbital (MO) Theory’. Storied names in chemistry like Pauling, Hǘckel and Pople are attached to this approach*

Assume the harmonic oscillator quantum system is to be modeled. Recall that its energy operator is:

$$\hat{ H}=H=\frac{-ħ^{2}}{2μ}\frac{d^{2}}{dx^{2}}+ \frac{1}{2}kx^{2} $$

Let’s approximate the ground state oscillator function:

 **φ = c1φ1 +c2φ2**

 **= c1 e- αx** + c2 e-2αx where α= (k/μ)1/2

For the sake of simplicity, let’s set k=μ=1 so that α=1 and let’s assume a unit system where $ħ=1$.

This means $\hat{ H}$ simplifies to become:

$$\hat{ H}= -\frac{1}{2}\frac{d^{2}}{dx^{2} } +\frac{1}{2}x^{2}$$

And since the exact energy of a harmonic oscillator has the form: E= ħω(n + ½) , n=0,1,2… with ω = (k/μ)1/2 =α, it means to exact lowest energy for our system at n=0 is:

**Eo(n=0, exact) = ½**

From **Supplement 8**, equation 4 the relevant problem to solve is to find Eφ =E that satisfies the determinant expression:

det H11 – ES11 H12-ES12 =0 **equation 1** **the secular determinant**

H21- ES21 H11-ES22

As already described in Supplement 8:

 H11 = <φ1|H|φ1> S11 = <φ1|φ1>

H12 =<φ1|H|φ2> S12 = S21 = <φ1|φ2> H21 = <φ2|H|φ1>

H22 = <φ2|H|φ2> S22 = <φ2|φ2>

Our job is four fold:

1. Compute the individual terms above
2. Plug them into the determinant and solve for E
3. Compare our `best E’ vs Eo to see if our guessed trial function is good or bad.
4. Back out the mixing coefficients c1 and c2 connected with the best E (not always necessary).

Answers to each step below are found in the attached appendix

**Step 1:** write down φ1 and φ2 given α=1 (it is common in MO theory to put in assumed constants for α that mimic a related system’s exact values)

φ1 = φ2 =

**Step 2:** Use Maple to compute the overlap integrals S11, S12 = S21 and S22

 (These are usually the `easy’ integrals)

  ∞

We have deliberately integrated over just 0🡪∞ here and for Hij whereas the actual oscillator requires -∞🡪+∞ . However, if we tried to use the e-ax function from 0🡪-∞, the integrals blow up. This means these functions are actually not viable choices given the rules for allowable φ, but to illustrate the process for a mathematically simple case, we have ignored the condition that φ satisfy boundary conditions. We thus will not necessarily obey the variational principle since our φ can’t actually be used in an analysis that must involve x= -∞🡪+∞

S11 = ∫φ1φ1 dx =

 0

 ∞

S22 = ∫φ2φ2 dx =

 0

 ∞

S12 = S21 = ∫φ1φ2 dx =

 0

**Step 3a:** compute **H**φ1 **and H**φ2 by hand. Note that $H=-\frac{1}{2}\frac{d^{2}}{dx^{2}}+ \frac{1}{2}x^{2} $since k=μ= ħ=1 here.

**H**φ1 = **H**φ2 =

**Step 3b:** multiply the above by either φ1 or φ2 to find:

φ1\* **H**φ1 = φ1\* **H**φ2=

φ2\* **H**φ1 = φ2\* **H**φ2=

**Step 4:** integrate the four terms above from 0🡪 ∞ using Maple to compute the related terms below:

 ∞

 ∞

H12 = ∫φ1\* **H**φ2 dx=

 0

H11 = ∫φ1\* **H**φ1 dx=

 0

 ∞

H22 = ∫φ2\* **H**φ2 dx=

 0

 ∞

H21 = ∫φ1\* **H**φ1 dx=

 0

**Step 5**: Plug the terms determined in steps 2 and 4 into the secular determinant (equation 1)

 H11-S11E H12-S12E

 Det = Det

 H21-S21E H22-S22E

**Step 6**: Expand the determinant by hand in the form (H11-ES11)(H22-ES22) – (H12-E12)(H21-E21)=0

 =0

**Step 7:** Plug the equation above into Maple, hit enter then select the entered equation, right click and `Solve’ for x….the positive quadratic solution is the correct `physical’ solution

Step 8: (optional) Back out the eigen vectors by plugging in the eigen values into the matrix and determining the relation of c1 to c2

Appendix

Step 1

φ1 = e-x φ2 = e-2x

Step 2

S11 = ½

S12 = 1/3

S22 = ¼

Step 3a

**H**φ1 =$-\frac{1}{2}e^{-x}+\frac{1}{2}x^{2}e^{-x}$ **H**φ2 = $-2e^{-2x}+\frac{1}{2}x^{2}e^{-2x}$

Step 3b

φ1\* **H**φ1 = $e^{-x}$\*($-\frac{1}{2}e^{-x}+\frac{1}{2}x^{2}e^{-x})$ φ1\* **H**φ2=$e^{-x}$\*($-2e^{-2x}+\frac{1}{2}x^{2}e^{-2x})$

φ2\* **H**φ1 = $e^{-2x}$($-\frac{1}{2}e^{-x}+\frac{1}{2}x^{2}e^{-x})$ φ2\* **H**φ2 = $e^{-2x}$($-2e^{-2x}+\frac{1}{2}x^{2}e^{-2x})$

Step 4

Integrating from 0🡪∞ the terms in step 3b we get:

**H11 = -1/8 H12 =-17/27**

**H21 = -7/54 H22 = -31/64**

Step 5: the secular determinant (x=E)

 H11-S11E H12-S12E -1/8 -x/2 -17/27 –x/3

 Det = Det

 H21-S21E H22-S22E -7/54 –x/3 -31/64 –x/4

Step 6:

The (unexpanded) algebraic equivalent = (-1/8 -x/2)( -31/64 –x/4) – (-7/54 –x/3)( -17/27 –x/3)=0

=(1/8 +x/2)( 31/64 +x/4) – (7/54 +x/3)( 17/27 +x/3)=0

Step 7:

The maple solution E=x=-211/288 ±(18929)0.5/96

The positive value is the only significant one

This has the the ~ value to 5 places of: 0.70056 vs 0.500 exact.

…so e‑x and e-2x are not great estimates of the Harmonic oscillator wavefunction…even if they `cheat’ by being disallowed.

Step 8 (optional)

If we wish to find the related eigen vectors (c1,c2), we must plug x=E back into the augmented form:

(-1/8 -0.70056/2) (-17/27-0.70056/3) 0

(-7/54-0.70056/3 (-31/64 -0.70056/4) 0

= -0.47528 -0.86315 0

 -0.36315 -0.65951 0

This is equivalent to

 -0.47528c1 -0.86315 c2 = 0

 -0.36315c1 -0.65951 c2 = 0

Either equation leads to the conclusion that c1 ~ -1.81c2 or c2 =-0.551c1

Since we want a normalized function:

1= c12S11 + c1c2S21 + c22S22

1=c12\* ½ -0.551c12\* 1/3 + (-0.551)2 c12\* ¼

1=0.39223c12

c1 = (1/0.39223)1/2 =1.596

c2 =-0.551c1 = -0.8797

Thus, the related `best’ wave function mixture producing a normalized φ is:

**φ= c1φ1 +c2φ2 = 1.596e-x - 0.8797e-2x where E = 0.70056 =eigen value**