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(*Jared Frazier*)
(*Variational-method-m6*)
(*Description:

Reproduction of variational principle findings from Physical Chemistry: A Molecular Approach (1997
with demonstrated trial functions.

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(*Date: 11/18/2020*)
Clear["Global`*"]
(*----------------------------------------------------*)
(*Question 1: Approximate Solution to Particle in 1D-box*)
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Print["
(*----------------------------------------------------*)
(*Question 1: Approximate Solution to Particle in 1D-box*)
(*----------------------------------------------------*)"]
Print["(1) Find the normalization constant A and assume L = 1"]
Print["(2) Normalization constant can be be found by
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$$\int_0^L |\phi|^2 dx = 1 \text{ where } \phi = Ax(x-L)\text{"]}$$

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Print["(3) Substituting ϕ into step (2),
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$$\int_0^L (Ax(x-L))^2 dx = A^2 \int_0^L x^2 (x-L)^2 dx = 1\text{"]}$$

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(*Definite integral calculation*)
L = 1; (*Length of box*)
phi = A*x*(x-L); (*Phi trial function without normalization const*)
closedIntegralPhiSquare = Integrate[phi^2, {x, 0, L}]; (*Result of integral*)
(*/Definite integral calculation*)

Print["(4) Using Mathematica to calculate the definite integral
where L = 1, ", closedIntegralPhiSquare, " = 1"]
Print["(5) Normalization constant A therefore is A = +-√30 "]
Print["(6)The Hamiltonian for a harmonic oscillator (particle
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$$\text{in a 1D-box) is given by } \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \text{ where } V(x) = 0$$

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in the bounds of the box 0 to L (L = 1)."]
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$$\text{Print["(7) } E_\phi = \frac{\langle \phi \mid \hat{H} \mid \phi \rangle}{\langle \phi \mid \phi \rangle} = \frac{\int_0^L \phi^* \hat{H} \phi dx}{\int_0^L |\phi|^2 dx} =$$

$$= \frac{\int_0^L Ax(x-L) - \frac{\hbar^2}{2m}\frac{d^2}{dx^2} Ax(x-L)\, dx}{1} = \frac{-\frac{\hbar^2}{2m}\int_0^L Ax(x-L)\frac{d^2}{dx^2} Ax(x-L)\, dx}{1}\text{"]}$$

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(*Second derivative of ϕ with respect to x and integral of phi*)
secondDerivPhi = D[phi, {x, 2}];
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closedIntegralPhi = Integrate[phi, {x, 0, L}];
(*/Second derivative of ϕ with respect to x*)

Print["(8) The second derivative with respect to x of the integral
in the denominator of step (6) is ", secondDerivPhi, "
then Eϕ = (-2A ℏ^2/(2m) ∫_0^L Ax(x-L) dx)/1 where the integral is ",
closedIntegralPhi, " then Eϕ = A^2ℏ^2/(6m) = 30h^2/(24mπ^2)"]

(*Calculation of Eϕ and Eo*)
h = Quantity["PlanckConstant"]; (*J/s*)
electronMass = Quantity["ElectronMass"]; (*kg*)
ePhi = (30*(h)^2)/(24*(electronMass)*Pi^2);
eNaught = ((h)^2)/(8*(electronMass));
(*/Calculation of Eϕ and E0*)

Print["(9) Using mathematica, Eϕ = ", N[ePhi, 4]]

Print["(10) This is a reasonable answer because Eϕ > E0, where E0 = π^2ℏ^2/(2mL^2) = ", N[eNaught, 4] ]

(*Calculation of percent error*)
percentError =N[(ePhi - eNaught)/eNaught * 100, 4];
(*/Calculation of percent error*)

Print["(11) Therefore, Eϕ = ", ePhi, " with ", percentError, "% error."]

(*---------------------------------------*)
(*Question 2: One parameter trial function*)
(*---------------------------------------*)
Print[
"\n(*---------------------------------------*)
(*Question 2: One parameter trial function*)
(*---------------------------------------*)"
]
Print["(1) First normalizing the function ϕ(α) = A(L^2- x^2)(L^2-αx^2) and using
∫_0^L |ϕ|^2dx = 1, therefore ∫_0^L (A(L^2- x^2)(L^2-αx^2))^2dx = 1"]

(*Normalization integral*)
phiAlpha = A*(L^2-x^2)(L^2-α*x^2); (*Without A*)
normIntegralPhiAlpha = Integrate[phiAlpha^2, {x, 0, L}];
(*/Normalization integral*)
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Print["(2) Using Mathematica, the result of integration is
", normIntegralPhiAlpha, " = 1"]

(*Solve for A*)
normConstant = Solve[normIntegralPhiAlpha == 1, A];
positiveNormConstant = A/.normConstant[[2]];
phiAlphaOnly = positiveNormConstant*(L^2-x^2)*(L^2-α*x^2); (*In terms of alpha, x, and L only*)
(*/Solve for A*)

Print["(3) Using Mathematica, the normalization constant
is A = ", positiveNormConstant]
Print["(4) Knowing the normalization constant,
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$$E(\alpha) = \frac{\langle \phi(\alpha) \mid \hat{H} \mid \phi(\alpha) \rangle}{\langle \phi(\alpha) \mid \phi(\alpha) \rangle} = \frac{\int_0^L (\phi(\alpha))^* \hat{H}\phi(\alpha)\,dx}{\int_0^L |\phi(\alpha)|^2 dx} = \int_0^L (\phi(\alpha))^* \hat{H}\phi(\alpha)\,dx"]$$

Print["(5) $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$ but $V(x) = 0$ in the 1D box, so substituting

$\hat{H}$ and $\phi(\alpha)$ into step (4), $E(\alpha) = -\frac{\hbar^2}{2m}\int_0^L$", phiAlphaOnly," $\frac{d^2}{dx^2}$", phiAlphaOnly, " dx"]

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(*Second derivative of ϕ with respect to x and integral of phiAlpha*)
secondDerivPhiAlpha = D[phiAlphaOnly, {x, 2}];
(*/Second derivative of ϕ with respect to x and integral of phiAlpha*)
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Print["(5) Second derivative inside the integrand is

$\frac{d^2}{dx^2}$", phiAlphaOnly, " = ", Simplify[secondDerivPhiAlpha], " The integral now becomes

$E(\alpha) = -\frac{\hbar^2}{2m}\int_0^L$", Simplify[phiAlphaOnly*secondDerivPhiAlpha], "dx"]

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(*Solution to integral*)
phiAlphaIntegrand = phiAlphaOnly*secondDerivPhiAlpha;
integralPhiAlpha = Integrate[phiAlphaIntegrand, {x, 0, L}];
(*/Solution to integral*)
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Print["(6) The result of that integral is E(α) = ", Simplify[$\frac{\text{-h\^{}2}}{\text{8*electronMass*Pi\^{}2}}$* integralPhiAlp

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(*Derivative ePhi with respect to α set to 0*)
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eAlpha = $\frac{\text{-h\^{}2}}{\text{8*electronMass*Pi\^{}2}}$ * integralPhiAlpha;

eAlphaFunc[α_] = $\frac{\text{-h\^{}2}}{\text{8*electronMass*Pi\^{}2}}$ * integralPhiAlpha;

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derivEAlpha = D[eAlpha, {α, 1}];
optimizedEAlpha = NSolve[derivEAlpha == 0, α];
alphaOne = α/.optimizedEAlpha[[1]];
alphaTwo = α/.optimizedEAlpha[[2]];
(*/Derivative ePhi with respect to α set to 0*)
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Print["(7) Then optimizing the parameter α, ∂E(α)/∂α = ", Simplify[derivEAlpha], " = 0" ]
Print["(8) α1 = ", N[alphaOne, 3], " or α2 = ", N[alphaTwo, 3]];
Print["(9) For α1 = ", N[alphaOne, 3], " E(α1) = ", eAlphaFunc[alphaOne]]
Print["    For α2 = ", N[alphaTwo, 3], " E(α1) = ", eAlphaFunc[alphaTwo]]

(*%error both instances*)
percentErrorAlpha1 = (eAlphaFunc[alphaOne] - eNaught)/eNaught*100;
(*/%error both instances*)

Print["(10) The optimal parameter value for this function must therefore be
α1 = ", alphaOne, " with corresponding energy E(α1) = ", eAlphaFunc[alphaOne]]

(*Residual Plot*)
exactPsi = Sqrt[2]*Sin[Pi*x];
phiOptimalAlphaOnly = phiAlphaOnly/.α→alphaOne;
Plot[
    {exactPsi-phiOptimalAlphaOnly, phiOptimalAlphaOnly,
    exactPsi},
    {x, 0, L}, PlotLabel→"Residual plot",
    AxesLabel→{"Length"}, PlotRange→Full, ImageSize→Large,
    PlotLegends→{"ψ1 - ϕ(α1,x)", "ϕ(α1,x)", "ψ1"}
]
(*----------------------------------*)
(*Question 3: Gaussian Trial Function*)
(*Pg 382 MCQ 2e*)
(*----------------------------------*)
Print[
"\n(*----------------------------------*)
(*Question 3: Gaussian Trial Function*)
(*----------------------------------*)"
]
Print["(1) Find normaliztion constant A of ϕ(r,α) = Ae^(-αr^2) using procedures
in previous steps (i.e. Denominator is < ϕ | ϕ > = ∫_-∞^∞ |ϕ|^2 r^2 dr = 1"]

(*Normalize the Gaussian*)
gaussian = A*Exp[-1*α*r^2]; (*Gaussian trial function*)
gaussianNormalizationIntegral = Normal[Integrate[r^2*gaussian^2, {r, 0, Infinity}]];
gaussianNormalizationConst = Simplify[A/.(Solve[gaussianNormalizationIntegral == 1, A])[[2]]];
normalizedGaussian = gaussian/.A→gaussianNormalizationConst;
(*/Normalize the Gaussian*)

Print["(2) The normalization constant A therefore is A = ", gaussianNormalizationConst]
Print["(3) Numerator of E(α) = ∫_0^∞ ϕ*Ĥϕr^2dr where Ĥ = -1/2 (d/dr^2 + 2/r d/dr) - 1/r"]

(*Hamiltonian operator*)
secondDerivGaussian = D[normalizedGaussian, {r, 2}];
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firstDerivGaussian = D[normalizedGaussian, {r, 1}];
divRGaussian = normalizedGaussian/r;
hamiltonianOnGaussian = -1/2*(secondDerivGaussian+2/r*firstDerivGaussian) - divRGaussian;
(*/Hamilitonian operator*)

Print["(4) Ĥϕ = -A/2(d/dr^2 ϕ + 2/r d/dr ϕ) - ϕ/r = ", Simplify[hamiltonianOnGaussian]]
Print["(5) Then E(α) = ∫_0^∞", Simplify[normalizedGaussian*hamiltonianOnGaussian], " r^2dr"]

(*Evaluate Hamiltonian with L = Infinity for hydrogen*)
eHAtom = Simplify[Normal[Integrate[normalizedGaussian*hamiltonianOnGaussian*r^2, {r, 0, Infinity}
(*/Evaluate Hamiltonian with L = Infinity for hydrogen*)

Print["(6) E(α) = ", eHAtom]

(*Optimize E(α)*)
firstDerivEHAtom = D[eHAtom, {α, 1}];
optimizedEHAtom = NSolve[firstDerivEHAtom == 0, α];
alphaEHAtom = α/.optimizedEHAtom[[1]];
functionEHAtom[a_] = -2*Sqrt[2/Pi]*Sqrt[a]+(3*a/2);
(*/Optimize E(α)*)
Print["(7) Optimization of E(α) => ∂E(α)/∂α = ", firstDerivEHAtom, " = 0"]
Print["(8) Optimal parameter for α = ", alphaEHAtom]
Print["(9) Minimum energy is E(α) = ", functionEHAtom[alphaEHAtom], ". This
is a reasonable value since E_min in the textbook is the same constant (-0.424) times
m_e e^4/(16π^2 ϵ_0^2 ħ^2) and E_0's constant is -0.500 times the m_e e^4/(16π^2 ϵ_0^2 ħ^2) for Gaussian trial function
for H-atom"]
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(*--------------------------------------------------*)
(*Question 1: Approximate Solution to Particle in 1D-box*)
(*--------------------------------------------------*)
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(1) Find the normalization constant A and assume L = 1

(2) Normalization constant can be be found by

$\int_0^L |\phi|^2 dx = 1$ where $\phi = Ax(x-L)$

(3) Substituting ϕ into step (2),

$\int_0^L (Ax(x-L))^2 dx = A^2 \int_0^L x^2 (x-L)^2 dx = 1$

(4) Using Mathematica to calculate the definite integral

where L = 1, $\frac{A^2}{30} = 1$

(5) Normalization constant A therefore is A = $+-\sqrt{30}$

(6) The Hamiltonian for a harmonic oscillator (particle in a 1D–box) is given by $\hat{H} = -\frac{\hbar^2}{2\,m}\frac{d^2}{dx^2} + V(x)$ where $V(x) = 0$ in the bounds of the box 0 to L (L = 1).

(7) $E_\phi = \frac{\langle \phi \mid \hat{H} \mid \phi \rangle}{\langle \phi \mid \phi \rangle} = \frac{\int_0^L \phi^* \hat{H}\,\phi dx}{\int_0^L |\phi|^2 dx} =$

$= \frac{\int_0^L Ax\,(x-L) - \frac{\hbar^2}{2\,m}\frac{d^2}{dx^2} Ax\,(x-L)\,dx}{1} = \frac{-\frac{\hbar^2}{2\,m}\int_0^L Ax\,(x-L)\,\frac{d^2}{dx^2} Ax\,(x-L)\,dx}{1}$

(8) The second derivative with respect to x of the integral in the denominator of step (6) is 2 A

then $E_\phi = \frac{-2\,A\,\frac{\hbar^2}{2\,m}\int_0^L Ax\,(x-L)\,dx}{1}$ where the integral is $-\frac{A}{6}$ then $E_\phi = \frac{A^2\,\hbar^2}{6\,m} = \frac{30\,h^2}{24\,m\pi^2}$

(9) Using mathematica, $E_\phi = 0.1267\,h^2/m_e$

(10) This is a reasonable answer because $E_\phi > E_0$, where $E_0 = \frac{\pi^2\,\hbar^2}{2\,mL^2} = 0.1250\,h^2/m_e$

(11) Therefore, $E_\phi = \frac{5}{4\,\pi^2}\,h^2/m_e$ with 1.321% error.

(*--*)
(*Question 2: One parameter trial function*)
(*--*)

(1) First normalizing the function $\phi(\alpha) = A(L^2 - x^2)(L^2 - \alpha x^2)$ and using $\int_0^L |\phi|^2 dx = 1$, therefore $\int_0^L (A(L^2 - x^2)(L^2 - \alpha x^2))^2 dx = 1$

(2) Using Mathematica, the result of integration is

$\frac{8}{315} A^2 \left(21 - 6\,\alpha + \alpha^2\right) = 1$

(3) Using Mathematica, the normalization constant

is $A = \frac{3\sqrt{\frac{35}{2}}}{2\sqrt{21 - 6\,\alpha + \alpha^2}}$

(4) Knowing the normalization constant,

$E(\alpha) = \frac{\langle \phi\,(\alpha) \mid \hat{H} \mid \phi\,(\alpha) \rangle}{\langle \phi\,(\alpha) \mid \phi\,(\alpha) \rangle} = \frac{\int_0^L (\phi\,(\alpha))^* \hat{H}\,\phi\,(\alpha)\,dx}{\int_0^L |\phi\,(\alpha)|^2 dx} = \int_0^L (\phi(\alpha))^* \hat{H}\phi(\alpha)\,dx$

(5) $\hat{H} = -\frac{\hbar^2}{2\,m}\frac{d^2}{dx^2} + V(x)$ but $V(x) = 0$ in the 1D box, so substituting

$\hat{H}$ and $\phi(\alpha)$ into step (4), $E(\alpha) = -\frac{\hbar^2}{2\,m}\int_0^L$

$$\frac{3\sqrt{\frac{35}{2}}\left(1 - x^2\right)\left(1 - x^2\,\alpha\right)}{2\sqrt{21 - 6\,\alpha + \alpha^2}}\;\frac{d^2}{dx^2}\,\frac{3\sqrt{\frac{35}{2}}\left(1 - x^2\right)\left(1 - x^2\,\alpha\right)}{2\sqrt{21 - 6\,\alpha + \alpha^2}}\;dx$$

(5) Second derivative inside the integrand is

$$\frac{d^2}{dx^2}\frac{3\sqrt{\frac{35}{2}}\left(1-x^2\right)\left(1-x^2\alpha\right)}{2\sqrt{21-6\alpha+\alpha^2}} = \frac{3\sqrt{\frac{35}{2}}\left(-1+\left(-1+6x^2\right)\alpha\right)}{\sqrt{21-6\alpha+\alpha^2}}$$ The integral now becomes

$$E(\alpha) = -\frac{\hbar^2}{2m}\int_0^L \frac{315\left(-1+x^2\right)\left(-1+x^2\alpha\right)\left(-1+\left(-1+6x^2\right)\alpha\right)}{4\left(21-6\alpha+\alpha^2\right)}dx$$

(6) The result of that integral is $E(\alpha) = \dfrac{\left(35-14\alpha+11\alpha^2\right)\left(\frac{3}{16\pi^2}h^2/m_e\right)}{21-6\alpha+\alpha^2}$

(7) Then optimizing the parameter α, $\dfrac{\partial E(\alpha)}{\partial\alpha} =$

$$\left(\left((-3+\alpha)\left(35-14\alpha+11\alpha^2\right)\left(-\frac{3}{2\pi^2}h^2/m_e\right)+(-7+11\alpha)\left(21-6\alpha+\alpha^2\right)\left(\frac{3}{2\pi^2}h^2/m_e\right)\right)\Big/(42+2(-6+\alpha)\alpha)^2\right) = 0$$

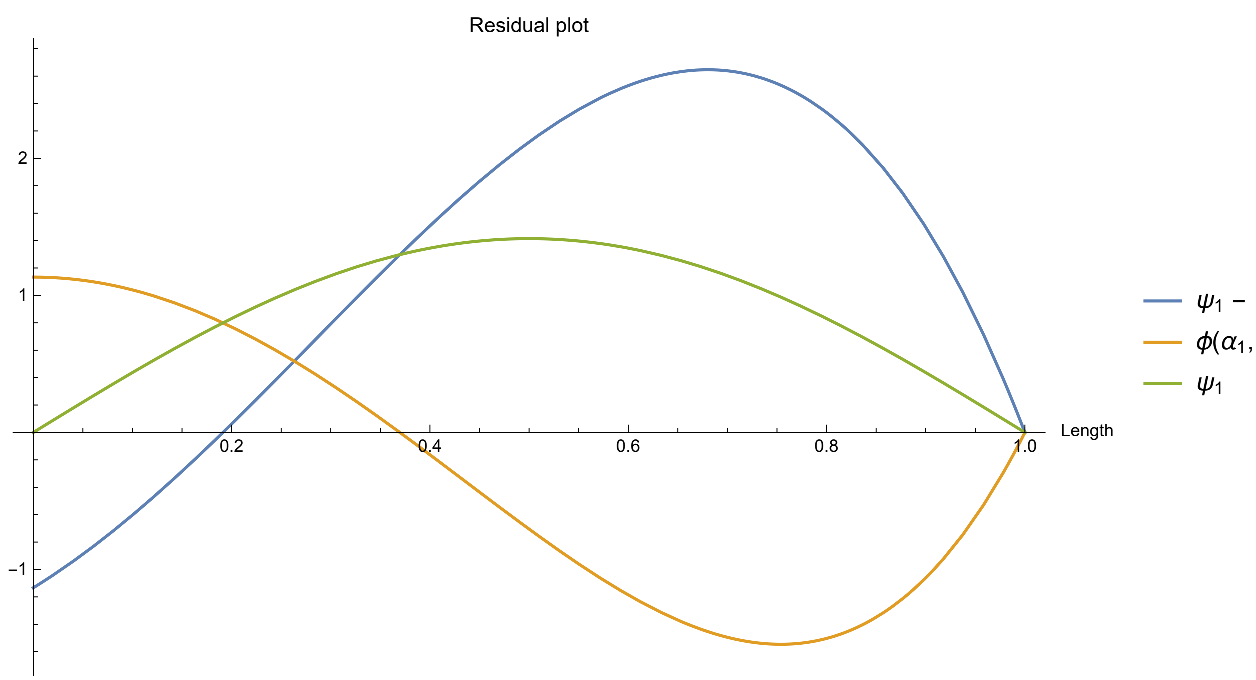
(8) $\alpha_1 = 7.32$ or $\alpha_2 = 0.221$

(9) For $\alpha_1 = 7.32$ $E(\alpha_1) = 0.323374\, h^2/m_e$

For $\alpha_2 = 0.221$ $E(\alpha_1) = 0.03125046\, h^2/m_e$

(10) The optimal parameter value for this function must therefore be
$\alpha_1 = 7.31771$ with corresponding energy $E(\alpha_1) = 0.323374\, h^2/m_e$

Out[746]=



(*----------------------------------*)
(*Question 3: Gaussian Trial Function*)
(*----------------------------------*)

(1) Find normaliztion constant A of $\phi(r,\alpha) = Ae^{-\alpha r^2}$ using procedures in previous steps (i.e. Denominator is $< \phi \mid \phi > = \int_{-\infty}^{\infty} |\phi|^2 r^2 dr = 1$

(2) The normalization constant A therefore is $A = \frac{2 \times 2^{3/4} \alpha^{3/4}}{\pi^{1/4}}$

(3) Numerator of $E(\alpha) = \int_0^{\infty} \phi^* \hat{H} \phi r^2 dr$ where $\hat{H} = -\frac{1}{2}\left(\frac{d}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) - \frac{1}{r}$

(4) $\hat{H}\phi = -\frac{A}{2}\left(\frac{d}{dr^2}\phi + \frac{2}{r}\frac{d}{dr}\phi\right) - \frac{\phi}{r} = -\frac{2 \times 2^{3/4} e^{-r^2 \alpha} \alpha^{3/4} \left(1 - 3 r \alpha + 2 r^3 \alpha^2\right)}{\pi^{1/4} r}$

(5) Then $E(\alpha) = \int_0^{\infty} -\frac{8 e^{-2 r^2 \alpha} \sqrt{\frac{2}{\pi}} \alpha^{3/2} \left(1 - 3 r \alpha + 2 r^3 \alpha^2\right)}{r} r^2 dr$

(6) $E(\alpha) = -2\sqrt{\frac{2}{\pi}}\sqrt{\alpha} + \frac{3\alpha}{2}$

(7) Optimization of $E(\alpha)$ => $\frac{\partial E(\alpha)}{\partial \alpha} = \frac{3}{2} - \frac{\sqrt{\frac{2}{\pi}}}{\sqrt{\alpha}} = 0$

(8) Optimal parameter for $\alpha = 0.282942$

(9) Minimum energy is $E(\alpha) = -0.424413$. This
is a reasonable value since E_{min} in the textbook is the same constant (-0.424) times $\frac{m_e e^4}{16 \pi^2 \epsilon_0^2 \hbar^2}$ and E_0's constant is -0.500 times the $\frac{m_e e^4}{16 \pi^2 \epsilon_0^2 \hbar^2}$ for Gaussian trial function for H-atom