7.E: Approximation Methods (Exercises)

Solutions to select questions can be found online.

7.3

Calculate the ground state energy of Harmonic Oscillator using variation method with the following trial wavefunction

$$\phi(x) = |\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

You may require these definite integrals:

$$\int_{-\infty}^{\infty} \frac{dx}{(1+\beta x^2)^n} = \frac{(2n-3)(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)(2n-6)\ldots(2)\cdot\pi/\beta^{1/2}}$$

$$\int_{-\infty}^{\infty} \frac{dx}{(1-\beta x^2)^n} = \frac{(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)\ldots(2)\cdot\pi/\beta^{3/2}}$$

Solution

First, we must know the Hamiltonian operator for the harmonic oscillator, which is

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

From this point on, the determination of $E_{ø}$ can be found using the trail function

$$|\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

which once substitute get the following equation for the numerator portion:

$$\int_{-\infty}^{-\infty} \frac{1}{(1+\text{\betax}^2)^2[\hbar^2/\mu * 2\beta/(1+\text{\betax}^2)^3 - \hbar^2/\mu * 12\beta^2x^2/(1+\text{\betax}^2)^4 + \frac{kx^2}{2}(1+\text{\betax}^2)^2]}$$

$$= 2\beta\hbar^2/\mu * (7*5*3*1*\pi/8*6*4*2*\beta 1/2) - 12\beta^2\hbar^2/\mu * (7*5*3*1*\pi/10*8*6*4*2*\beta 1/2) + k/2 * (3*1*\pi/6*4*2*\beta^{3/2})$$

$$= \frac{7\pi\beta^{1/2}\hbar}{32\mu + k\pi/32\beta^{3/2}}$$

Now solving the denominator:

$$\int_{\infty}^{\infty} \phi^*\phi\, dx = \int_{\infty}^{\infty} \frac{1}{(1+\beta x^2)^4} = \frac{5*3*1*\pi}{6*4*2*\beta^{1/2}} = \frac{5\pi}{/16\beta^{1/2}}$$

After this we will find

$$E_\phi = \frac{7\pi\beta^{1/2}\hbar^2}{32\mu * (16\beta^{1/2}/5\pi)} + \frac{k\pi}{32\beta^{3/2} * (16\beta^{1/2}/5\pi)} = \frac{7/10 * \beta\hbar 2}{\mu} + \frac{1}{10}\frac{k}{\beta}$$

Then find minimum value

\dfrac{dE_\phi}{d \beta}= \dfrac{7 \hbar^2}{10µ} -\dfrac{ k}{10 \beta^2_{min} = 0\nonumber

therefore

$$\beta_{min} = \sqrt{\frac{\mu k}{7\hbar^2}}$$

\[E_{min}= \dfrac{7^{1/2} \hbar }{5 * (k/µ)^{1/2}} + \dfrac{7^{1/2} \hbar }{5 (k/µ)^{1/2} }= 71/2 \hbar /5 (k/µ)$^{1/2}$ = 0.53 \hbar *(k/µ)$^{1/2\nonumber}$ \]

Therefore overall get

$$E_{exact} = 0.500\hbar\sqrt{(k/\mu)}$$

⇒ this value differs by 6%.

7.8

What is the variational (trial) energy of the trial function

$$|\phi\rangle = e^{-ax^2}$$

for the ground-state of a harmonic oscillator? Just set up the integral, but do not evaluate. Use

$$\hat{H} = \frac{\hbar^2}{2m}\nabla n^2 + \frac{kx^2}{2}$$

Solution

The variational energy:

$$E_{trial}(a) = \frac{\langle\phi(a)|\hat{H}|\phi(a)\rangle}{\langle\phi(a)|\phi(a)\rangle} \geq E_{true}$$

numerator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-2ax^2}\,dx$$

All combined together to extract the trial energy as a function of a:

$$E_{trial}(a) = \frac{\int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2(e^{-ax^2})}{dx^2} + \frac{kx^2}{2}\right] e^{-ax^2}\,dx}{\int_{-\infty}^{\infty} e^{-2ax^2}\,dx}$$

Use the components of $\hat{H}$ to operate on ϕ

$$\langle\phi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}\right] e^{-ax^2}\,dx$$

denominator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2} e^{-ax^2}\,dx$$

7.9

Use the trial function

$$|\exp^{\frac{-\alpha x^2}{2}}\rangle$$

to set up the integrals to find the ground state energy of a anharmonic oscillator whose potential is $V(x) = cx^5$, but do not evaluate.

Solution

$$E = \frac{\int_{-\infty}^{\infty}\phi^*\hat{H}\phi d\tau}{\int_{-\infty}^{\infty}\phi^*\phi d\tau}$$

$$\int_{-\infty}^{\infty}\phi^*\phi d\tau = \int_{-\infty}^{\infty}\exp^{-\alpha x^2}\,dx$$

$$\int_{-\infty}^{\infty}\phi^*\hat{H}\phi d\tau = \int_{-\infty}^{\infty}\left(\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5\right)\exp^{-\alpha x^2}\,dx$$

$$E = \frac{\int_{-\infty}^{\infty}\left(\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5\right)\exp^{-\alpha x^2}\,dx}{\int_{-\infty}^{\infty}\exp^{-\alpha x^2}\,dx}$$

7.12

Consider a particle of mass m in a box from $x=-a$ to $x=a$ with $V(x)=-V_0$ for $|x|\geq a$. Assume a trial function of the form

$$|\phi(x)\rangle = l^2 - x^2$$

for $-l<x<l$ and $\psi(x)=0$ otherwise. l is the parameter. Does the trial function satisfy the requirements of a particle in a box wavefunction?

The result of the variational method was

$$E_\phi(s)=\frac{5}{16}\frac{\hbar^2}{ma^2}\left[\frac{4}{s^2}+\frac{4}{5}\left(8-\frac{15}{s}+\frac{10}{s^3}-\frac{3}{s^5}\right)\right]$$

Where $s=\dfrac{l}{a}$ is a new variational parameter for convenience of expression. Derive a polynomial expression for s that can be solved to obtain the value of s that yields the ground state energy, but do not attempt to solve for this value of s .

Solution

Yes, it is finite over all x values, it's first and second derivatives are continuous, and it meets the boundary conditions $\psi(-a)=\psi(a)=0$, and it is normalizable for a choice of l.

Taking the derivative of E with respect to s,

$$\frac{\partial E}{\partial s}=0=-\frac{8}{s^3}+\frac{4}{5}\left(\frac{15}{s^2}-\frac{30}{s^4}+\frac{15}{s^6}\right)$$

With some algebra, this becomes,

$$3s^4-2s^3-6s^2+3=0$$

With a calculator or other root finding procedure, s can be solved for.

7.13

Given a trial wavefunction equal to sin $\lambda(x)$, explain in words a stepwise procedure on how you would go about solving for the energy of this trial wavefunction as well as how to minimize the error.

Solution

1. Denote $\sin(\lambda(x))=\phi_n$
2. Solve the integral $\langle\phi_n^*|\phi_n\rangle$
3. Solve the integral $\langle\phi_n^*|\hat{H}|\phi_n\rangle$
4. Now that you solved for steps 2 and 3, plug into the equation

$$E_n=\frac{\langle\phi_n^*|\hat{H}|\phi_n\rangle}{\langle\phi_n^*|\phi_n\rangle}$$

5. Take the derivative of E_n with respect to λ and set equal to 0.

$$\frac{dE_n}{d\lambda}$$

6. Solve for λ and plug back into equation in step 4.

7.16

Using the variational method approximation, find the ground state energy of a particle in a box using this trial function:

$$|\phi\rangle = N\cos\left(\frac{\pi x}{L}\right)$$

How does is it compare to the true ground state energy?

Solution

The problem asks that we apply variational methods approximation to our trial wavefunction.

$$E_{\phi} = \frac{\langle \phi|\hat{H}|\phi\rangle}{\langle \phi|\phi\rangle} \geq E_o$$

$$\langle \phi|\phi\rangle = 1 = \int_0^L N^2\cos^2\left(\frac{\pi x}{L}\right)$$

Performing this integral and solving for N yields

$$N = \sqrt{\frac{2}{L}}$$

The Hamiltonian for a particle in a one dimensional box is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}\langle \phi|\hat{H}|\phi\rangle &= \langle N\cos\left(\frac{\pi x}{L}\right)\Big|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big|N\cos\left(\frac{\pi x}{L}\right)\rangle \\ &= \int_0^L N\cos\left(\frac{\pi x}{L}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}N\cos\left(\frac{\pi x}{L}\right)dx \\ &= \frac{N^2\pi^2\hbar^2}{2mL^2}\int_0^L \cos^2\left(\frac{\pi x}{L}\right)dx\end{aligned}$$

where $N = \sqrt{\frac{2}{L}}$. The above equation after the integral becomes

$$\frac{\pi^2\hbar^2}{mL^3}\left(\frac{L}{2}\right)$$

$$E_{\phi} = \frac{\pi^2\hbar^2}{2mL^2}$$

This is equal to the ground state energy of the particle in a box that we calculated from the Schrodinger equation using

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

7.17

For the three-electron detrimental wavefunction

$$\psi = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \end{vmatrix}.$$

confirm that:

a. the interchange of two columns changes the sign of the wavefunction,
b. the interchange of two rows changes the sign of the wavefunction, and
c. the three electrons cannot have the same spin orbital.

Solution

First find the determinant

$$\psi = \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(2) \\ \phi_C(1) & \phi_C(2) \end{vmatrix}$$

$$= \phi_A(1)\ (\phi_B(2)\phi_C(3) - \phi_C(2)\phi_B(3)) - \phi_A(2)\ (\phi_B(1)\phi_C(3) - \phi_C(1)\phi_B(3)) + \phi_A(3)\ (\phi_B(1)\phi_C(2) - \phi_C(1)\phi_B(2))$$

$$\psi = \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(3)\phi_B(1)\phi_C(2) - \phi_A(3)\phi_C(1)\phi_B(2)$$

a) Switch column 1 with column 2

$$\psi_{(a)} = \begin{vmatrix} \phi_A(2) & \phi_A(1) & \phi_A(3) \\ \phi_B(2) & \phi_B(1) & \phi_B(3) \\ \phi_C(2) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(a)} = \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(2) & \phi_B(1) \\ \phi_C(2) & \phi_C(1) \end{vmatrix}$$

$$\phi_{(a)} = \phi_A(2)\phi_B(1)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) + \phi_A(1)\phi_C(2)\phi_B(3) + \phi_A(3)\phi_B(2)\phi_C(1) - \phi_A(3)\phi_C(2)\phi_B(1)$$

Comparing equation (5) with equation (6) we see that $\phi = -\phi_{(a)}$

b) Switch row 2 with row 3

$$\phi_{(b)} = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \end{vmatrix}.$$

Now find the determinant

$$\phi_{(b)} = \phi_A(1) \begin{vmatrix} \phi_C(2) & \phi_C(3) \\ \phi_B(2) & \phi_B(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_C(1) & \phi_C(3) \\ \phi_B(1) & \phi_B(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_C(1) & \phi_C(2) \\ \phi_B(1) & \phi_B(2) \end{vmatrix}$$

$$\phi_{(b)} = \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(3)\phi_C(1)\phi_B(2) - \phi_A(3)\phi_B(1)\phi_C(2)$$

Comparing equation (5) with equation (7) we see that $\phi = -\phi_{(b)}$

c) Replace column 2 with column 1

$$\phi_{(c)} = \begin{vmatrix} \phi_A(1) & \phi_A(1) & \phi_A(3) \\ \phi_B(1) & \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(c)} = \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(1) \\ \phi_C(1) & \phi_C(1) \end{vmatrix}$$

The first two terms are identical but opposite so they cancel one another. The third has a determinant of zero.

$$\phi_{(c)} = 0 + \phi_A(3) \cdot (0) = 0$$

7.20

a. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for an oscillator that has a potential of

$$V(x) = (1/2)kx^2 + x^3 + x^4 + x^5?$$

b. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a particle in a box that has a potential of $V(x) = 0$ between 0<x<L?

c. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a hydrogenlike atom that has a potential of

$$V(x) = \frac{-e^2}{4\pi\epsilon_o r} + \frac{1}{2}\epsilon r \cos\theta?$$

Solution

For an oscillator:

$$\hat{H} = \frac{-\hbar 2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2 + x^3 + x^4 + x^6$$

$\hat{H}^{(0)}$ is the Hamiltonian for a simple harmonic oscillator, therefore

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2$$

$\hat{H}^{(1)}$ is what is added to the Hamiltonian for a simple harmonic oscillator. therefore

$$\hat{H}^{(1)} = x^3 + x^4 + x^5$$

$\Psi^{(0)}$ is the wave function for a simple harmonic oscillator, therefore

$$\Psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$E^{(0)}$ is the energy for a simple harmonic oscillator, therefore

$$E^{(0)} = h\nu\left(v + \frac{1}{2}\right)$$

where v= 0,1, 2... ∞

Particle in a box

Using this as an example, we find that for a particle in a box with potential V(x) = 0 between 0<x<L

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\hat{H}^{(0)} = -\frac{\hbar 2}{2m}\frac{\partial^2}{\partial x^2}$$

\[\hat{H}^{(1)} = 0\nonumber \]

$\Psi^{(0)}$ =B*sin(nπx/L)

$E^{(0)} = n^2h^2 / 8mL^2$ where n= 1, 2, 3 ... ∞

Hydrogen like Atom

For a hydrogen like atom that has a potential of

$$V(x) = -\frac{e^2}{4\pi\epsilon_o r} + (1/2)\epsilon r\cos\theta$$

\[\hat{H} = - ħ ^{2}/2μ ∂2 /∂x2 ∇^2 -$e^2/(4\pi\epsilon_o r)$ + (1/2)ϵrcosθ\nonumber \]

\[\hat{H}$^{(0)}$ = - ħ ^{2}/2μ ∂2 /∂x2 ∇^2 -$e^2/(4\pi\epsilon_o r)$\nonumber \]

\[\hat{H}$^{(1)}$ =(1/2)ϵrcosθ\nonumber \]

$\Psi^{(0)} = \Psi_{n,l,m}(r,\theta,\phi)$

$E^{(0)} = \mu e^4 / 8\epsilon_o^2h^2n^2$

7.21

Using a harmonic oscillator as the unperturbed problem, calculate the first-order correction to the energy of the $v = 0$ level for the system described as

$$V(x) = \frac{k}{2}x^2 + \frac{m}{6}x^3 + \frac{b}{24}x^4$$

7.22

Using the first order perturbation theory for particle in a box, calculate the ground-state energy for the system

$$V(x) = ax^3 \qquad 0 < x < b$$

Solution

$$\psi_1 = \sqrt{\frac{2}{b}}\sin(\frac{\pi \mathrm{x}}{b})$$

$$\widehat{H} = \widehat{H}^0 + \widehat{H}^1$$

$$\widehat{H}^1 = ax^3$$

$$E_1 = E_1^0 + E_1^1$$

$$E_1^0 = \frac{h^2}{8mb^2}$$

$$E_1^1 = \langle \psi^1 | \widehat{H}^1 | \psi^1 \rangle$$

$$= \int_0^b \frac{2a}{b}x^3 \sin^2(\frac{\pi \mathrm{x}}{b})\mathrm{dx}$$

$$= \frac{2a}{b}\frac{(\pi^2 - 3)b^4}{8\pi^2}$$

$$= \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

$$E_1 = \frac{h^2}{8mb^2} + \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

7.23

In your chemistry lab you were able to manipulate an external electric field to have the strength κ. You're supervisor wants you to figure out what the first-order correction to the ground state energy of a hydrogen like atom of charge N in this electric field.

Solution

You should remember, or look up the ground state wavefunction for a hydrogen atom and find that

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{Z_\circ}\right)^{\dfrac{3}{2}} e^{-r/a_o}$$

Our change in energy equation has a familiar form

$$\Delta E = \int \psi^{(0)*}\,\hat{H}^{(1)}\,\psi^{(0)}\,d\tau$$

For this problem you construct a Hamiltonian for a Hydrogen atom in an electron field with strength κ.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ne^2}{4r\pi\kappa_\circ} + er\kappa\cos\theta$$

Luckily you have previously calculated $\hat{H}^{(1)}$ for this system in a previous experiment, simply allowing you to substitute your variables into your expressions to find that

$$\Delta E = \frac{Ne\kappa}{\pi}\left(\frac{1}{Z_\circ}\right)^3 \int_0^\infty r^3 e^{\dfrac{-r}{a_\circ}}\,dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\cos\theta d\theta$$

Notice that the problem gets simplified by the fact that

$$\int_0^\pi \sin\theta\cos\theta d\theta = 0$$

So your answer is a trivial solution.

$$\boxed{\Delta E = 0}$$

7.25A

Use first-order perturbation theory to calculate ground-state energy of a harmonic oscillator with a cx^7 added to the end of the potential.

Solution

The Hamiltonian to the system can be formulated as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^7$$

we then solve

$$E^1 = \langle \psi_0 | cx^7 | \psi_0 \rangle$$

We know that the integral is of an odd function over a symmetric boundary is 0, so by symmetry we can conclude that the energy is 0.

7.25B

In order to calculate the first-order correction to the ground-state energy of the quartic oscillator, use first-order perturbation theory. The potential energy is $V(x) = cx^4$. For this potential use the harmonic oscillator as the unperturbed system. Solve for the perturbing potential as well.

Solution

The Hamiltonian operator is given below:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

To use a harmonic oscillator as the reference system, add and subtract $\frac{1}{2}kx^2$ from $\hat{H}$.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d}{dx^2} + \frac{1}{2}kx^2 \ + cx^4 - \frac{1}{2}kx^2$$

Hence we get :

$$\hat{H}^{(0)} = cx^4 - \frac{1}{2}kx^2$$

Now we have:

$$\Delta\text{E} = \int \psi^{(0)*}\, \hat{H}^{(1)}\, \psi^{(0)}\ d\tau \ .\ .\ .\ .$$

By putting the values in the equation above, we get:

$$\begin{aligned}\Delta E &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-x^2\alpha} \left(cx^4 - \frac{1}{2}kx^2\right) \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} 2\left[\frac{3c}{8\alpha^2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{k}{8\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}\right] \\ &= \frac{3c}{4\alpha^2} - \frac{k}{4\alpha}\end{aligned}$$

7.26

Solve the following integrals using this trial wavefunction

$$|\phi\rangle = c_1 x(a-x) + c_2 x^2(a-x)^2$$

For simplicity purposes, we can assume that a = 1.

$$H_{11} = \frac{\hbar^2}{6m} \;\; S = \frac{1}{30}$$

$$H_{12} = H_{22} = \frac{\hbar^2}{30m} \;\; S_{12} = S_{21} = \frac{1}{140}$$

$$H_{22} = \frac{\hbar^2}{105m} \;\; S_{22} = \frac{1}{630}$$

Solution

We know that for a particle in a box

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

We also know the two components of the trial function that was given are

$$\phi_1 = x(a-x)$$

and

$$\phi_2 = x^2(a-x)^2$$

Using this we will have

$$\hat{H}\phi_1 = \frac{\hbar^2}{2m}$$

and

$$\hat{H}\phi_2 = \frac{\hbar^2}{m}(a^2 - 6ax + 6x^2)$$

Using this we can solve for H_{ii} and S_{ij} using this integral

$$\int_0^1 x^m(1-x)^n dx = \frac{m!n!}{(m+n+1)!}$$

Letting $a = 1$, we can now solve for

$$H_{11} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)dx = \frac{\hbar^2}{6m}$$

$$H_{12} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)(1-6x+6x^2)dx = \frac{\hbar^2}{30m}$$

$$H_{21} = \frac{\hbar^2}{m}$$

$$\int_0^1 x^2(1-x)^2 dx = \frac{\hbar^2}{30m}$$

$$H_{22} = \frac{\hbar^2}{105m}$$

$$S_{11} = \int_0^1 x^2(1-x)^2 dx = \frac{4}{5!} = \frac{1}{30}$$

$$S_{12} = S_{21} = \int_0^1 x^3(1-x)^3 dx = \frac{36}{7!} = \frac{1}{140}$$

$$S_{22} = \int_0^1 x^4(1-x)^4 dx = \frac{576}{9!} = \frac{1}{630}$$

7.27

Use Perturbation Theory to add cubic and quartic perturbations to the SHO and find the first three SHO energy levels. Do this by expanding the Morse potential:

$$V(x) = D(1 - e^{-Bx})^2$$

into polynomials (i.e., a Taylor expansion). Show that the Hamiltonian can be written as

$$\frac{-h^2\nabla^2}{8\pi^2 m} + ax^2 + bx^3 + cx^4$$

Note which terms can be associated with H^0 and which are the H^1 perturbation. What are the relationships between a, b, c, and D, B? How do the new energy levels compare to the old ones?

Solution

The e^{-Bx} function can be expanded noting that

$$e^x \approx 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \ldots + Ox^n$$

So e^{-Bx} will expand similarly, replacing x in the above expansion with -Bx, so

e^{-Bx] = 1 - Bx + B^2x^2/2 - B^3x^3/6 + ... + Ox^n\nonumber

The Morse Potential therefore is

$$D(1 - (1 - Bx + B^2\frac{x^2}{2} - B^3\frac{x^3}{6})^2$$

The expansion is shortened to 4 terms only.

$$= D(Bx - B^2x^2/2 + B^3x^3/6)^2$$

$$=D (B^6x^6/36 - B^5x^5/6 + 7B^4x^4/12 - B^3x^3 + B^2x^2)$$

$$= DB^6x^6/36 - DB^5x^5/6 + 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

$$= 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

(We have truncated above the quartic term)

Here, it is seen that DB^2x^2 corresponds to the H^0 potential, and $7DB^4x^4/12 - DB^3x^3$ is H^1

We can also see that $a = DB^2$, $b = - DB^3$, $c = 7DB^4/12$ in in the Hamiltonian potential: $ax^2 + bx^3 + cx^4$

Perturbation theory states that

$$E_n = E_n^0 + E_n^1 = E_n^0 + \int \Psi_n^0 H^1 \Psi_n^0 \, d\tau$$

Therefore, with $E^0_0 = h\nu/2$ and $\Psi^0_0 = (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}$

$E^0_1 = 3h\nu/2$ and $\Psi^0_1 = (4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}$

$E^0_2 = 5\, h\nu/2$ and $\Psi^0_2 = (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}$

$H^1 = bx^2 + cx^2$

the first three energy levels are:

$E_0 = h\nu/2 + \int (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}(bx^3 + cx^4)(\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}dx$

$= h\nu/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}(bx^3 + cx^4)dx$

$= h\nu/2 + (\alpha/\pi)^{1/2} [\int e^{-\alpha(x^2)}bx^3dx + \int e^{-\alpha(x^2)}cx^4dx]$ (The cubic integral is odd so evaluates to 0)

$= h\nu/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}cx^4dx$

We can use $\int x^{2n}e^{-\alpha x^2}dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= h\nu/2 + 2 * c(\alpha/\pi)^{1/2} * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}$

$= h\nu/2 + 3c/(4\alpha^2)$

$E_1 = 3h\nu/2 + \int(4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}(bx^3 + cx^4)(4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} \int x^2e^{-\alpha(x^2)}(bx^3 + cx^4)dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} [\int x^2e^{-\alpha(x^2)} bx^3dx + \int x^2e^{-\alpha(x^2)} cx^4dx]$ (First integral evaulates to 0)

$= 3h\nu/2 + c(4\alpha^3/\pi)^{1/2} \int x^6e^{-\alpha(x^2)} dx$

We can use $\int x^{2n}e^{-\alpha x^2}dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 3h\nu/2 + 2^* c(4\alpha^3/\pi)^{1/2} {}^* 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2}$

$= 3h\nu/2 + 15c/(4\alpha^2)$

$E_{2o} = 5h\nu/2 + \int (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}(bx^3 + cx^4) (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2}\int(bx^3 + cx^4)(2\alpha x^2 - 1)^2e^{-\alpha(x^2)}dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2}[\int bx^3(2\alpha x^2 - 1)^2e^{-\alpha(x^2)}dx + \int cx^4e^{-\alpha(x^2)}(2\alpha x^2 - 1)^2dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2}\int cx^4e^{-\alpha(x^2)}(2\alpha x^2 - 1)^2dx$ (First integral evaulates to 0)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2}\int 4c\alpha^2x^8e^{-\alpha(x^2)} - 4\alpha cx^6e^{-\alpha(x^2)} + cx^4e^{-\alpha(x^2)}dx$

We can use $\int x^{2n}e^{-\alpha x^2}dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2}[4c\alpha^2*2*(105/(32\alpha^4))* (\pi/\alpha)^{1/2} - \alpha c*2*15/(2^4\alpha^3) * (\pi/\alpha)^{1/2} + c*2*3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}]$

$= 5h\nu/2 + 39c/4\alpha^2$

It is evident that as the energy levels increase, the perturbation to the energy increases as well, making the Hooke potential increasingly bad as an approximation of intramolecular potential.

7.27

Use the perturbation theory to calculate the first - order corrections to the ground state energy of

a. A harmonic oscillator that arises from a cubic and quartic term.
b. A quartic oscillator that arises from only using a quartic term cx^4

and compare the results.

Solution

A) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = bx^3 + cx^4$$

$$\psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$$E^{(0)} = h\mu(v + \frac{1}{2})$$

$$E_0 = E_0^{(0)} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E_0 = \frac{\hbar\mu}{2} + b(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^3 e^{-x^2\alpha} + c(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + 0 + 2c\frac{\alpha}{\pi}^{1/2}\int_0^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + \frac{3c}{4\alpha^2}$$

B) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = cx^4 - \frac{kx^2}{2}$$

$$E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E = (\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}(cx^4 - \frac{kx^2}{2})$$

$$E = (\frac{\alpha}{\pi})^{1/2}2(\frac{3c}{8\alpha^2}(\frac{\alpha}{\pi})^{1/2} - \frac{k}{8\alpha}(\frac{\alpha}{\pi})^{1/2})$$

$$E = \frac{3c}{4\alpha^2} + \frac{k}{4\alpha}$$