Nov. 19 2007

Chem. 1410

Problem Set 9, due Nov. 28, 2007

The following problem is to be handing in for grading:

1) Variational Principle (Linear Variation of Parameters) for Perturbed Particle in a 1D Box. A particle of mass *m* moves in a 1D box with infinite potential walls at x=0 and x=L. Inside the box, the particle experiences a linear potential, namely, $w(x) = k(x - L/2)$. Thus, the complete potential energy function governing the motion of the system is:

$$V(x) = \begin{cases} \infty & , x \le 0 \\ w(x), & 0 < x < L \\ \infty & , x \ge 0 \end{cases} \qquad [1]$$

In this problem we'll use the Variational Principle with linear parameter variation to obtain an upper bound on the ground state energy of this system.

First, recall some properties of a particle in the standard infinite box ($w(x) = 0$). Specifically: energy eigenvalues are given by $E_n = n^2 E_{gs}^{PB}$, *n=1,2,3,...* with $E_{gs}^{PB} \equiv \frac{\hbar^2 \pi^2}{2mL^2}$ being the ground state energy (again, for the standard particle in the box). The corresponding normalized eigenfunctions are $\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$.

To treat the modified particle in a box potential specified in Eq. 1, we consider the variational trial function:

$$\psi_T(x) = c_1\phi_1(x) + c_2\phi_2(x)$$

The goal is to determine $c_{1,2}$ (s.t. $c_1^2 + c_2^2 = 1$) so as to minimize the expectation value $< \psi_T | \hat{H} | \psi_T >$, where $\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ with $V(x)$ given in Eq. 1. This will give a variationally optimized approximation to the ground state energy of $\hat{H}$ (plus a concomitant approximation to the corresponding ground state energy eigenfunction).

Appealing to the linear variation of parameters version of the Variational Principle, we need to solve the eigenvalue/eigenvector problem:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad [2]$$

with the Hamiltonian matrix elements given by $H_{ij} = T_{ij} + V_{ij}$, where

$$T_{ij} = -\frac{\hbar^2}{2m}\int_0^L dx\phi_i(x)\frac{\partial^2}{\partial x^2}\phi_j(x) \quad , V_{ij} = -\frac{\hbar^2}{2m}\int_0^L dx\phi_i(x)w(x)\phi_j(x)$$

Now:

a) Why do no " S_{ij} " basis function overlap factors appear in Eq. 2?

b) Show that the kinetic energy matrix elements are given by:

$$\begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} = E_{gs}^{PB} \begin{bmatrix} 1 & 0 \\ 0 & 4 \end{bmatrix} \qquad [3]$$

c) By doing the relevant integrals it can be shown (you do not have to do this here!) that the potential matrix is given by:

$$\begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} = -\frac{16}{9\pi^2} kL \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad [4]$$

d) By adding together Eqs. 3,4, show that:

$$\boldsymbol{H} \equiv \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = E_{gs}^{PB} \begin{bmatrix} 1 & -\gamma \\ -\gamma & 4 \end{bmatrix} \qquad [5]$$

with the dimensionless parameter $\gamma \equiv \frac{16}{9\pi^2}\frac{kL}{E_{gs}^{PB}}$. Note that γ is a measure of the strength of the internal potential $w(x)$ since $\gamma \propto k$ (all other parameters being held fixed).

e) Derive a formula for the eigenvalues of $\boldsymbol{H}$. The lower value corresponds to the variationally optimized ground state of $\hat{H}$. Denote this eigenvalue as E_{GS} : plot $E_{GS}(\gamma)/E_{gs}^{PB}$ in the range of coupling strengths

$-1 < \gamma < 1$. Is the ground state energy for this "perturbed" potential (with the linear trough in the middle, as specified in Eq. 1) higher or lower than that of the standard particle in a box (corresponding to $\gamma = 0$)?

f) Calculate the eigenvector that corresponds to the ground state energy eigenvalue determined in part e): specifically, determine the ratio c_2 / c_1 as a function of γ.

g) For the value $\gamma = 0.5$, plot the normalized ground state wavefunction associated with the variational trial function which we have studied here on the same graph with the ground state energy eigenfunction of the standard 1D particle in the box ($\gamma = 0$). Can you explain why the ground state wavefunction should look as it does (compared to that of the unperturbed particle in a box)? [Hint: Plot the potential function, too!]