Chem. 1410, Problem Set 9; solution key.

1) a) The two basis functions are orthogonal, and are unit-normalized. That is, $\int dx\phi_i(x)\phi_j(x) = \delta_{ij}$ for $i = 1,2$. [Recall that δ_{ij} is the Kronecker delta: $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.] Thus, the overlap matrix **S** becomes the 2x2 unit matrix and "disappears" from the problem.

b) Using the property: $\frac{-\hbar^2}{2m}\frac{\partial^2\phi_j(x)}{\partial x^2} = j^2 E_{gs}^{PB}\phi_j(x)$, *j=1,2*, then: $H_{jk} = E_{gs}^{PB} j^2 \delta_{jk}$.

c) By straightforward addition, one obtains:

$$\boldsymbol{H} \equiv \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} + \begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} = E_{gs}^{PB}\begin{bmatrix} 1 & -\gamma \\ -\gamma & 4 \end{bmatrix}$$

d)The eigenvalues of $\boldsymbol{H}$ are $E_{1,2} = E_{gs}^{PB}\lambda_{1,2}$, where $\lambda_{1,2}$ are the two roots of the quadratic equation:

$$(1-\lambda)(4-\lambda) - \gamma^2 = 0$$

Thus,

$$\lambda_1 = \frac{5-\sqrt{9+4\gamma^2}}{2} \quad , \lambda_2 = \frac{5+\sqrt{9+4\gamma^2}}{2}$$

Obviously, $\lambda_1 < \lambda_2$, and hence:

$$E_{GS}(\gamma)/E_{gs}^{PB} = \frac{5-\sqrt{9+4\gamma^2}}{2}$$

A plot of $E_{GS}(\gamma)/E_{gs}^{PB}$ is shown in Fig. 1: clearly, this ratio is less than 1 for any non-zero value of the perturbation γ. The ground state energy of this system is thus *lowered* from the standard particle in the box value for any non-zero value of γ.

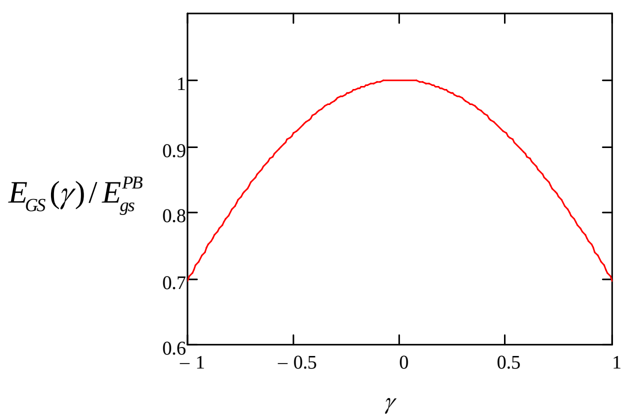

Fig. 1

e) We seek the eigenvector $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ arising from the matrix equation:

$$E_{gs}^{PB}\begin{bmatrix} 1 & -\gamma \\ -\gamma & 4 \end{bmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{gs}^{PB}\lambda_1\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad \text{[A1]}$$

This vector is specified by the ratio:

$$r = c_2 / c_1 = 2\gamma / (3 + \sqrt{9 + 4\gamma^2})$$

[Note: The ratio c_2 / c_1 is uniquely determined by Eq. [A1], but the absolute value is not.]

f) The approximation to the unit-normalized ground state eigenfunction arising from the trial function adopted here is thus:

$$\psi_{GS}(x) = \frac{1}{\sqrt{1+r^2}}[\phi_1(x) + r\phi_2(x)]$$

For the value $\gamma = 0.5$, $\psi_{GS}(x)$ is plotted vs. $\phi_1(x)$ in Fig. 2. Note that with a linear trough $w(x) = k(x - L/2)$ in the internal region of the box [note: $w(x)$ has a positive slope when k (or γ) is positive], the ground state eigenfunction shifts so as to "sit in" the trough (where the potential is lower) to some degree.

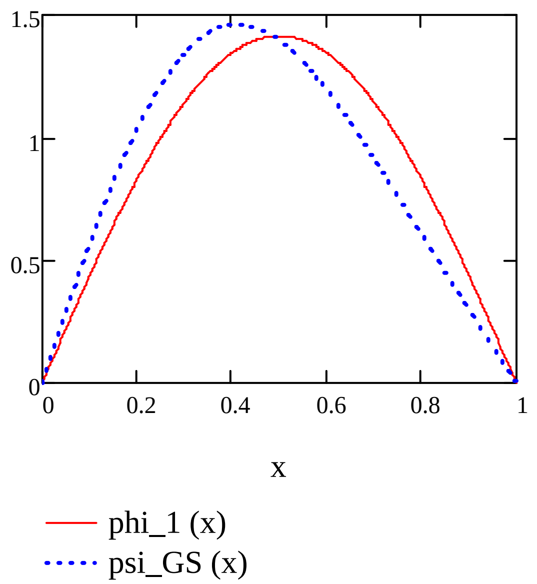

Fig. 2. For the value $\gamma = 0.5$, $\psi_{GS}(x)$ is plotted vs. $\phi_1(x)$.