1. Consider a particle in a one-dimensional box of length L, with Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \qquad 0 < x < L.$$

Infinite potential energy outside the box requires that the wavefunction $\psi(x)$ vanishes at the boundaries: $\psi(x) = 0$ for $x \leq 0$ and $x \geq L$.

(i) The box length L is a natural unit of distance for this problem, so let's define a dimensionless coordinate $x^* = x/L$. What choice of energy scale ϵ will give the simple dimensionless Hamiltonian

$\frac{dx^*}{dx} = 1/L$

$$\mathcal{H}^* = \mathcal{H}/\epsilon = -\frac{d^2}{dx^{*2}} \quad ?$$

For the rest of the problem we will use this unitless description. Asterisks on $\mathcal{H}$ and x will be implied, energies will implicitly have units of ϵ, and distances will have units of L.

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad \frac{d^2}{dx^2} = -\frac{1}{L^2}\frac{d^2}{dx^{*2}}.$$

$$= -\frac{\hbar^2}{2mL^2}\frac{d^2}{dx^{*2}}$$

$$\rightarrow H^* = H \cdot \frac{2mL^2}{\hbar^2} = -\frac{d^2}{dx^{*2}}.$$

$$\epsilon = \hbar^2/2mL^2$$

(ii) Wavefunctions for a particle in a box have the form

$$\psi_n(x) = A\sin(n\pi x), \quad \text{for} \quad 0 \leq x \leq 1,$$

where A is a constant, and n can be any positive integer. Show that $\psi_n(x)$ is indeed a solution to Schrödinger's equation, $\hat{\mathcal{H}}\psi_n(x) = E_n\psi_n(x)$. Determine its energy E_n.

$$H\psi_n(x) = -\frac{d^2}{dx^2}(A\sin(n\pi x))$$

$$= An^2\pi^2\sin(n\pi x).$$

$$E_n = n^2\pi^2$$

In normal units: $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

(i) We call $G(\lambda, x_0)$ a generating function because its derivatives generate useful information. For example, if we calculate the first derivative of G with respect to λ (holding x_0 fixed) and then set $\lambda = 0$, we find

$$\left.\frac{dG}{d\lambda}\right|_{\lambda=0} = \langle\phi_A|(x - x_0)|\phi_B\rangle.$$

Use a similar approach to relate $\langle\phi_A|(x - x_0)^2|\phi_B\rangle$ to a derivative of G.

$$\left.\frac{d^2G}{d\lambda^2}\right|_{\lambda=0} = \langle\phi_A|(x-x_0)^2|\phi_B\rangle$$

(ii) How could you obtain the quantity $\langle\phi_A|\phi_B\rangle$ from $G(\lambda, x_0)$?

$$G(\lambda, x_0) = \langle\phi_A| e^{\lambda(x-x_0)} |\phi_B\rangle$$

$$\rightarrow G(0, x_0) = \langle\phi_A|\phi_B\rangle.$$

(iii) The generating function $G(\lambda, x_0)$ can be evaluated by straightforward but tedious integration, which we will spare you. The result is

$$G(\lambda, x_0) = \sqrt{\frac{\pi}{2\alpha}} \exp\left[-\frac{\alpha}{2}(x_A - x_B)^2 + \frac{\lambda}{2}(x_A + x_B - 2x_0) + \frac{\lambda^2}{8\alpha}\right]. \tag{2}$$

Using Eq. 2 and your result from part (ii), show that the overlap between two basis functions is

$$S_{AB} \equiv \int_{-\infty}^{\infty} dx\, \phi_A^*(x)\phi_B(x) = \sqrt{\frac{\pi}{2\alpha}}\, e^{-\alpha(x_A - x_B)^2/2}$$

$$S_{AB} = G(0, x_0)$$

$$= \sqrt{\pi/2\alpha}\, \exp\left(-\frac{\alpha}{2}(x_A - x_B)^2\right).$$

(iv) Using Eq. 2 and your result from part (i), show that

$$\langle \phi_A | (x - x_0)^2 | \phi_B \rangle = \frac{S_{AB}}{4}\left[(x_A + x_B - 2x_0)^2 + \frac{1}{\alpha} \right]$$

$$\langle \phi_A | (x - x_0)^2 | \phi_B \rangle = \left.\frac{\partial^2 G}{\partial \lambda^2}\right|_{\lambda=0} .$$

$$\dots := x_A + x_B - 2x_0 .$$

$$\rightarrow \frac{d}{d\lambda}\left(\sqrt{\pi/2\alpha} \left(\frac{(x_A + x_B - 2x_0)}{2} + \frac{2\lambda}{8\alpha} \right) \cdot \exp\left(-\frac{\alpha}{2}(x_A - x_B)^2 + \frac{\lambda}{2}(\dots) + \frac{\lambda^2}{8\alpha} \right) \right)$$

$$= \sqrt{\pi/2\alpha} \left(\frac{2}{8\alpha} \right) \exp\left(-\frac{\alpha}{2}(x_A - x_B)^2 + \frac{\lambda}{2}(\dots) + \frac{\lambda^2}{8\alpha} \right)$$

$$+ \left(\frac{(x_A + x_B - 2x_0)}{2} + \frac{2\lambda}{8\alpha} \right)^2 \exp\left(-\frac{\alpha}{2}(x_A - x_B)^2 + \frac{\lambda}{2}(\dots) + \frac{\lambda^2}{8\alpha} \right))$$

$$= \left.\left(\sqrt{\pi/2\alpha} \exp\left(-\frac{\alpha}{2}(x_A - x_B)^2 + \frac{\lambda}{2}(\dots) + \frac{\lambda^2}{8\alpha} \right) \right) \left(\frac{2}{8\alpha} + \frac{(x_A + x_B - 2x_0)^2}{4} + \lambda \dots \right)\right|_{\lambda=0}$$

$$= \left(\sqrt{\pi/2\alpha} \right) \left(S_{AB} \right) \left(\frac{1}{4} \right) \left((x_A + x_B - 2x_0)^2 + 1/\alpha \right).$$

$\blacksquare$

(v) Show that

$$\left(-\frac{d^2}{dx^2}+x^2\right)\phi_A(x)=\left[x^2+2\alpha-4\alpha^2(x-x_A)^2\right]\phi_A(x)$$

$$\phi_A = e^{-\alpha(x-x_A)^2}$$

$$\frac{d^2}{dx^2}\phi_A = \frac{d}{dx}\left(-2\alpha(x-x_A)e^{-\alpha(x-x_A)^2}\right)$$

$$= -2\alpha x e^{-\alpha(x-x_A)^2} + (-2\alpha(x-x_A))^2 e^{-\alpha(x-x_A)^2}$$

$$= e^{-\alpha(x-x_A)^2}\left(-2\alpha + 4\alpha^2(x-x_A)^2\right)$$

$$\rightarrow -\frac{d^2}{dx^2}\phi_A + x^2\phi_A = \left(2\alpha - 4\alpha^2(x-x_A)^2 + x^2\right)\phi_A .$$

(vi) Now combine the results of parts (iii), (iv), and (v) to calculate matrix elements of the Hamiltonian operator $\mathcal{H}=(-d^2/dx^2+x^2)/2$:

$$\mathcal{H}_{AB}=\frac{S_{AB}}{2}\left[\alpha+\frac{1}{4\alpha}+\frac{1}{4}(x_A+x_B)^2-\alpha^2(x_A-x_B)^2\right] \tag{3}$$

$$H_{AB} = \frac{1}{2}\langle\phi_A| -\frac{d^2}{dx^2}+x^2 |\phi_B\rangle$$

$$= \frac{1}{2}\langle\phi_A| 2\alpha - 4\alpha^2(x-x_B)^2 + x^2 |\phi_B\rangle$$

$$= \frac{1}{2}\left(2\alpha\langle\phi_A|\phi_B\rangle - 4\alpha^2\langle\phi_A|(x-x_B)^2|\phi_B\rangle + \langle\phi_A|x^2|\phi_B\rangle\right)$$

$$= \frac{1}{2}\left(2\alpha S_{AB} - 4\alpha^2\left(\frac{S_{AB}}{4}\left[(x_A-x_B)^2+1/\alpha\right]\right) + \frac{S_{AB}}{4}\left[(x_A+x_B)^2+1/\alpha\right]\right)$$

$$= \frac{S_{AB}}{2}\left(\alpha - \alpha^2(x_A-x_B)^2 + \frac{(x_A+x_B)^2}{4} + 1/4\alpha .\right)$$