Mathematica Exercise: Variational Theory

Physical Chemistry I
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1. The variational theorem states for any trial function φ that meets the boundary conditions of the problem, the variational energy can be computed from

$$E_{\text{var}} = \frac{\int \varphi^* \hat{H} \varphi d\tau}{\int \varphi^* \varphi d\tau}$$

and is an upper bound to the true ground state energy for the problem, that is

$$\frac{\int \varphi^* \hat{H} \varphi d\tau}{\int \varphi^* \varphi d\tau} \geq E_o$$

This formulation does not require the trial function to be normalized. Why?

2. Consider the following three trial functions for the one-dimensional particle in the box. The box has length *a*. Normalize the functions. Are all of them appropriate trial functions, once normalized?

a. $\varphi(x) = x(a - x)$

b. $\varphi(x) = x\sqrt{\frac{1}{a^3}}$

b. $\varphi(x) = x^2(a^2 - x^2)$

3. Which one of the (appropriate) trial functions is best? That is, which one gives the closest value to the true energy?

4. Using each of the (appropriate) trial functions, compute the average value of the position, *x*. Which of the trial functions is best by this measure? Can you understand why? Hint: Plot the trial functions and the true function.

5. Use the trial function

$$\varphi(x) = x^\alpha(a^2 - x^2) \text{ where } \alpha \in \mathbb{R} \text{ and } \alpha > 1$$

α is an adjustable parameter. Find the value for α that gives the best value of the energy. Hint: Don't use the **Solve** command in Mathematica for this, instead, consider a graphical solution. How does this compare with the value of the energy for the normalized version of the trial function in 2.b.?