

Quantum Chemistry

Exercises 7B

1. Suppose one were to use a trial function of the form

$$\phi(r) = c_1 e^{-\alpha r} + c_2 e^{-\beta r^2}$$

to carry out a variational calculation for the ground state of the hydrogen atom. Can you guess without doing any calculations what c_1 , c_2 , α , and E_{min} will come out to be?

2. Approximate the solution of the particle-in-a-box problem 1b of Exercise set 7A by the vibrational principle using the trial functions given below, with c_1 and c_2 as variables:

a.
$$\phi(x) = c_1 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right) + c_2 \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a} x\right)$$

b.
$$\phi(x) = c_1 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right) + c_2 \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a} x\right)$$

- c. Compare and discuss the results of these calculations and those done using perturbation theory and by solving the problem numerically.