1 Problem 1

In previous discussion, we have considered approximate methods for obtaining energies, wavefunctions, or both for quantum systems more complicated than the Hydrogen atom. In this exercise, consider the quantum harmonic oscillator and use the variational principle to evalute the ground state wavefunction and the ground state energy.

Use the following normalized trial wavefunction:

$$\chi = \left(\frac{\gamma}{\pi}\right)^{\frac{1}{4}} e^{-\gamma x^2/2} \qquad \gamma = \textit{variational parameter}$$

The Hamiltonian for the one-dimensional quantum harmonic oscillator is:

$$\hat{H} = \frac{-\hbar^2}{2\,\mu}\frac{d}{dx^2} + \frac{kx^2}{2}$$

You are free to use your handbook of equations for evaluating necessary integrals.

1.1 Solution

The one-dimensional harmonic oscillator:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{kx^2}{2}$$

Let's consider a trial wavefunction:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{kx^2}{2}$$

Trial wavefunction:

$$\chi = \left(\frac{\gamma}{\pi}\right)^{1/4} e^{-\gamma x^2/2}; \qquad \gamma \; variable \; (variational \; parameter)$$

$$E_{var} = \int \chi^* \hat{H} \chi d\mathbf{r} = \left(\frac{\gamma}{\pi}\right)^{1/2} \int e^{-\gamma x^2/2} \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{kx^2}{2}\right) e^{-\gamma x^2/2} dx$$

$$= -\frac{\hbar^2}{2\mu}\left(\frac{\gamma}{\pi}\right)^{1/2} \left[\int_{-\infty}^{\infty} \gamma e^{-\gamma x^2} dx + \int_{-\infty}^{\infty} (\gamma x)^2 e^{-\gamma x^2} dx\right] + \frac{k}{2}\left(\frac{\gamma}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\gamma x^2} dx = \frac{\hbar^2 \gamma}{4\mu} + \frac{k}{4\gamma} \geq E_o$$

Now, allow γ to **vary** and optimize E_{var}:

$$\frac{dE_{var}}{d\gamma} = \frac{\hbar^2}{4\mu} - \frac{k}{4\gamma^2} = 0$$

$$\gamma = \frac{(k\mu)^{1/2}}{\hbar} \equiv \alpha$$

This leads, with no surprise, to the exact solutions to the 1-D H.O.

$$\chi = \psi_o(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \rightarrow \quad E_{var} = \frac{\hbar\omega}{2} = E_o$$

2 Problem 2

What is the general expression for the first order perturbation correction to the ground state energy of a system with perturbation Hamiltonian $\hat{H}_1$?

2.1 Solution

$$E_o^1 \ = \ \int_{all\ \ space} \psi_0^* \ \hat{H}_1 \ \psi_0 \ d^3\mathbf{r}$$

3 Problem 3

What are the effective nuclear charges "seen" by electrons in the $1s$, $2s$, and $2p$ atomic orbitals for the carbon atom? What is the true nuclear charge for this system?

3.1 Solution

1s = 5.67
2s = 3.22
2p = 3.14