CHM 428 Assignment 5

April 18, 2022

Due 22^{nd} April, 2022

1. Consider the one-particle, 1-dimensional system with potential energy
   $V(x) = V_0$ for $\frac{1}{4}L < x < \frac{3}{4}L$,
   $V(x) = 0$ for $0 \leq x \leq \frac{1}{4}L$ and $\frac{3}{4}L \leq x \leq L$,
   and $V(x) = \infty$ everywhere else, where $V_0 = \hbar^2/mL^2$.

   (a) Using the trial wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(\pi x/L)$ for $0 \leq x \leq L$, estimate the ground-state energy and compare with the true ground state energy $5.750345\hbar^2/mL^2$.

   (b) The trial wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(2\pi x/L)$ for $0 \leq x \leq L$ gives an upper bound to the energy of the first excited state in the above problem. Explain why. Also estimate the upper bound to the first excited state and compare with true value $20.23604\hbar^2/mL^2$.

2. Consider the one-particle, 1-dimensional system with potential energy
   $V(x) = V_0$ for $\frac{1}{4}L < x < \frac{3}{4}L$,
   $V(x) = 0$ for $0 \leq x \leq \frac{1}{4}L$ and $\frac{3}{4}L \leq x \leq L$,
   and $V(x) = \infty$ everywhere else, where $V_0 = \hbar^2/mL^2$. Treating the system as a perturbed particle in a 1-d box,

   (a) Find the first-order correction to the energy for the general stationary state with quantum number n.

   (b) For the ground and first excited states, compare $E^{(0)} + E^{(1)}$ with the true energies $5.750345\hbar^2/mL^2$ and $20.23604\hbar^2/mL^2$, respectively. Explain why $E^{(0)} + E^{(1)}$ for each of these two states is the same as obtained by the variation principle in the previous problem.

3. A particle in a spherical box of radius b has $V = 0$ for $0 \leq r \leq b$ and $V = \infty$ for $r > b$. Use the trial function $\phi = b - r$ for $0 \leq r \leq b$ and $\phi = 0$ for $r > b$ to estimate the ground state energy and compare with the true value $h^2/8mb^2$.

4. For the hydrogen atom, use the Gaussian trial function $\phi = e^{-cr^2/a_0^2}$ to estimate the ground-state energy. Determine the best value of c that will yield the lowest variational estimate for the energy.

5. Consider a H_2^+ molecular ion in the Born-Oppenheimer approximation with equilibrium bond length R_0 in the ground-state. For the single electron in the system, use the trial wavefunction $\psi = c_1\phi_{1s}(\vec{r} - \vec{R}_1) + c_2\phi_{1s}(\vec{r} - \vec{R}_2)$ to estimate the ground state energy, thereby determining the best c_1 and c_2. Here, $\phi_{1s}(\vec{r})$ is the $1s$ orbital wavefunction and $\vec{R}_i$ refers to the position of the ith proton.

6. For a hydrogen atom placed in an electric field $E_0\hat{k}$, determine the first order corrected energies of the first and second shell levels.

7. A particle confined to move freely along a ring of radius R is perturbed by a potential of the form $V(\phi) = V_0 cos(\phi)$. Using first order perturbation theory determine the changes in the energies and wavefunctions of the ground ($m = 0$) and first excited levels ($m = \pm 1$).