PG SEMESTER-III (PHYSICAL CHEMISTRY SPECIALIZATION)
TIME-INDEPENDENT NON-DEGENERATE RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY
ASSIGNMENT 1 (14/09/2024)

1. Assume that the charge of the proton is distributed uniformly throughout the volume of a sphere of radius 10^{-13} cm. Use perturbation theory to estimate the shift in the ground-state hydrogen-atom energy due to the finite proton size. The potential energy experienced by the electron when it has penetrated the nucleus and is at distance r from the nuclear centre is $-eQ/4\pi\varepsilon_0 r$, where Q is the amount of charge on the proton within the sphere of radius r. [The evaluation of the integral is simplified by noting that the exponential factor in ψ is essentially equal to 1 within the nucleus.]

2. For an anharmonic oscillator with $\hat{H} = -(\hbar^2/2m)(d^2/dx^2) + kx^2/2 + cx^3$, take cx^3 as the perturbation.
   (a) Evaluate the first-order correction to energy for the state with quantum number v.
   (b) Evaluate the second-order correction to energy for the state with quantum number v.
   (c) Which unperturbed states contribute to $\psi_v^{(1)}$?

3. Consider a one particle, one dimensional system with $V = V_0$ for$(0.25 + c)l < x < (0.75 + c)l$, $V = 0$ for $0 \leq x \leq (0.25 + c)l$ and$(0.75 + c)l \leq x \leq l$, and $V = \infty$ elsewhere. V_0 and c are constants and $0 \leq c \leq 0.25$. (i) Take the unperturbed system as a particle in a one-dimensional box and find$E^{(1)}$ in terms ofV_0 and c. (ii) Plot $E^{(1)}/V_0$ versus c for the ground state.

4. Consider a one particle, one dimensional system with $V = \infty$ for $x < 0$ and for $x > l$ and $V = C$ for $0 \leq x \leq$ l, where C is a constant. (i) Sketch V for $C > 0$. (ii) Treat the system as a perturbed particle in a box and find $E_n^{(1)}$ for the state with quantum number n.

5. Calculate the energy of the nth excited state to first-order perturbation theory for a spin-less particle of mass m moving in an infinite potential well of length $2L$, with the walls at $x = 0$ and $x = 2L$:
$$V(x) = \begin{cases} 0 & 0 \leq x \leq 2L \\ \infty & \text{otherwise} \end{cases},$$
which is modified at the bottom by the perturbation, $V_p(x) = \lambda V_0 \sin(\pi x/2L)$.
6. Show that the first-order non-degenerate stationary-state Rayleigh-Schrödinger perturbation theory always overestimates the ground state energy.
7. A one-dimensional simple harmonic oscillator was perturbed using a linear potential of the form $q\mathcal{E}X$. Using a suitable variable transformation, calculate the exact energy for the perturbed state of the system.
8. Deduce an expression, using suitable transformation(s), for the Hamiltonian operator for the hydrogen atom in atomic units.
9. Show that there is no linear Stark effect for the hydrogen atom.
10. Show, using the occupation number representation, that the first-order correction to energy in a one-dimensional simple harmonic oscillator is zero.