PG SEMESTER-III (PHYSICAL CHEMISTRY SPECIALIZATION)
PROBLEMS ON DEGENERATE-STATE PERTURBATION THEORY
ASSIGNMENT 3 (08/10/2024)

1. A certain unperturbed system has a doubly degenerate energy level for which the perturbation integrals have the values $V_{11} = 4b$, $V_{12} = 2b$, $V_{22} = 6b$, where b is a positive constant, $V_{ij} = \left\langle \psi_i^{(0)} \middle| V \middle| \psi_j^{(0)} \right\rangle$, and $\left\langle \psi_i^{(0)} \middle| \psi_j^{(0)} \right\rangle = \delta_{ij}$. (a) In terms of b, find the $E^{(1)}$ values for the perturbed system. (b) Find the normalized correct zeroth-order wave functions. (c) Explain why without solving for the $E^{(1)}$ values, we can be certain that the sum of the $E^{(1)}$ values is $10b$.
2. For a particle in a square box of length l with origin at $x = 0$, $y = 0$, write down the wave functions and energy levels. If the system is perturbed by
$$V = b, \text{for} \frac{1}{4}l \leq x \leq \frac{3}{4}l \text{ and } \frac{1}{4}l \leq y \leq \frac{3}{4}l$$
where b is a constant and $V = 0$ elsewhere, find $E^{(1)}$ for the ground state. For the first excited energy level, find the $E^{(1)}$ values and the correct zeroth-order wave functions.
3. Using the first-order (degenerate) perturbation theory, calculate the energy levels of the $n = 2$ states of a hydrogen atom placed in an external uniform weak electric field along the positive z-axis.
4. If the spin effects are neglected, the four states of the hydrogen atom with $n = 2$ have the same energy E^0. Show that, when an electric field, $\mathcal{E}$ is applied to hydrogen atoms in these states, the resulting first-order energies are $E^0 \pm 3a_0 e\mathcal{E}$, E^0 and E^0.